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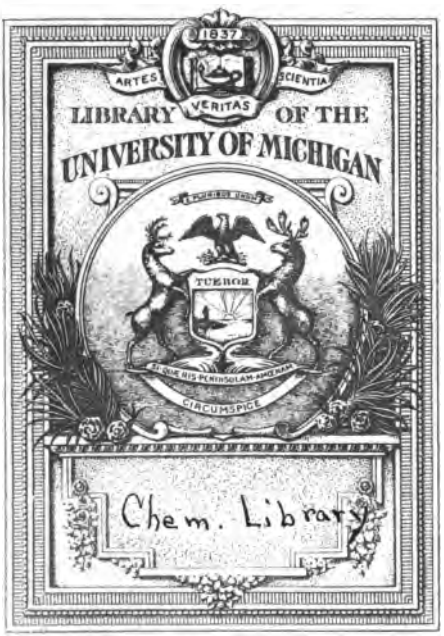

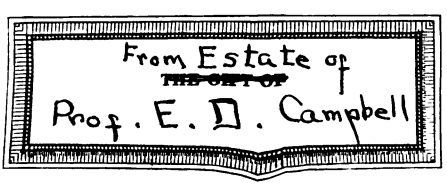

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PRINCIPLES

OF

THEORETICAL

CHEMISTRY,

WITH SPECIAL REFERENCE TO THE

CONSTITUTION OF CHEMICAL COMPOUNDS.

BY

IRA REMSEN,

PROFESSOR OF CHEMISTRY IN THE JOHNS HOPKINS UNIVERSITY.

SECOND EDITION, THOROUGHLY REVISED AND ENLARGED.

PHILADELPHIA:
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PREFACE TO SECOND EDITION.

THE title of this book is somewhat vague. I have endeavored to discuss in an impartial way, as objectively as possible, the principal hypotheses which at present play important parts in the science of chemistry. As, strictly speaking, we have no theory of chemistry, the hypotheses are more or less disconnected; and as there is no general theory to keep them in check, some of them have assumed a variety of forms. My object has been to point out, as clearly as I could, the exact connection between the facts known to us and the hypotheses.

Much harm has been done the science by a too free use of hypotheses by those who were ignorant of the facts which suggest them. This has been and is particularly noticeable in connection with the use of structural or constitutional formulas. It is heart-rending to see a tyro in chemistry using these formulas with a freedom that might well appal one who knows their true meaning. An experience of years with students of chemistry has led me to the conclusion that the formulas are generally used without understanding. To do something towards correcting this serious evil is my earnest desire.

The book has been thoroughly revised, and much of it has been entirely rewritten. The principal changes will be found in the chapters on valence and constitution. These have been materially changed, and, I believe, much improved. A short chapter on the physical methods for determining the constitution of chemical compounds has been added.

I. R.

BALTIMORE, November, 1883.

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LIST OF ELEMENTS AND ATOMIC WEIGHTS.

Name of Element.	Symbol.	Atomic weight.	Atomic weight very accurately determined.
Aluminum,	Al	27	27.009
Antimony,	Sb	120	119.955
Arsenic,	As	75	74.918
Barium,	Ba	136.8	136 763
Bismuth,	Bi	207.5	207.523
Boron,	B	10.9	10.941
Bromine,	Br	79.8	79.768
Cadmium,	Cd	111.8	111.835
Cæsium,	Cs	132.6	132.583
Calcium,	Ca	40	39.99
Carbon,	C	12	11.9736
Cerium,	Ce	140.4	140.424
Chlorine,	Cl	35.4	35.37
Chromium,	Cr	52	52.009
Cobalt,	Co	58.9	58.887
Columbium,	Cb	93.8	93.812
Copper,	Cu	63.2	63.173
Didymium,	Di	145.4	145.4
Erbium,	E	166	165 891
Fluorine,	F	19	18.984
Gallium,	Ga	70	69.9
Glucinum,	Gl	9	9.085
Gold,	Au	196.2	196.155
Hydrogen,	H	1	1
Indium,	In	113.4	113.398
Iodine,	I	126.6	126 557
Iridium,	Ir	192.7	192.651
Iron,	Fe	56	55.913
Lanthanum,	La	138.5	138.526
Lead,	Pb	206.5	206.471
Lithium,	Li	7	7.0073
Magnesium,	Mg	24	23.959
Manganese,	Mn	54	53.906
Mercury,	Hg	199.7	199.712
Molybdenum,	Mo	95.5	95.527
Nickel,	Ni	58	57.928
Nitrogen,	N	14	14.021

LIST OF ELEMENTS AND ATOMIC WEIGHTS.—*Continued.*

Name of Element.	Symbol.	Atomic weight.	Atomic weight very accurately determined.
Osmium,	Os	198.5	198.494
Oxygen,	O	16	15.9633
Palladium,	Pd	105.7	105.737
Phosphorus,	P	31	30.958
Platinum,	Pt	194.4	194.415
Potassium,	K	39	39.019
Rhodium,	Rh	104	104.055
Rubidium,	Rb	85.3	85.251
Ruthenium,	Ru	104.2	104.217
Samarium,	Sm	150	150.021
Scandium,	Sc	44	43.98
Selenium,	Se	78.8	78.797
Silicon,	Si	28.2	28.195
Silver,	Ag	107.7	107.7
Sodium,	Na	23	22.998
Strontium,	Sr	87.4	87.374
Sulphur,	S	32	31.984
Tantalum,	Ta	182	182.144
Tellurium,	Te	128	127.96
Thallium,	Th	203.7	203.715
Thorium,	Th	233.4	233.414
Tin,	Sn	117.7	117.698
Titanium,	Ti	49.8	49.846
Tungsten,	W	183.6	183.61
Uranium,	U	239.8	239.8
Vanadium,	V	51.3	51.256
Ytterbium,	Yb	172.8	172.761
Yttrium,	Y	89.8	89.816
Zinc,	Zn	65	64.9045
Zirconium,	Zr	89.4	89.367

PRINCIPLES

OF

THEORETICAL CHEMISTRY.

PART FIRST.

GENERAL DISCUSSION OF ATOMS AND MOLECULES.

I.

COMBINING NUMBERS—ATOMIC WEIGHTS—ATOMIC HYPOTHESIS.

General Conceptions.—Substances that occur in nature are, for the most part, not simple substances. They can generally be decomposed into kinds of matter that are unlike—some in one way, some in another. Such substances are called compound. In regard to the means required to separate these compounds into their constituents, a marked difference is noticed in different cases. In some cases simple mechanical processes only are required to effect the separation. In others, it is found that, after the application of all purely mechanical processes has failed, the compounds yield to the influence of some of the so-called physical forces, as heat, light, electricity. This leads to the conclusion that there are at least two kinds of compound substances. Each of these kinds is more or less strongly characterized by external properties. As regards those which can be decomposed by mechanical means alone, it is true that they possess the combined properties of their constituents; and these constituents are usually contained in the compound in their original forms. As regards the second class of compounds, on the other hand, it is just as true that they do not possess the properties of their constituents;

and these constituents are contained in the compounds in forms differing entirely from those originally possessed by them.

Chemism.—Particles of matter are held together in different ways, and special names have been introduced to designate these different ways. Thus we have the names adhesion and cohesion, the former referring to the mutual attraction of bodies in contact with one another, and the latter referring to the attraction exerted between particles of the same kind, as between particles of iron, copper, water, etc. So far as particles are held together by adhesion or cohesion, they can be separated by mechanical means. But particles may be held together in another way and then they cannot be separated by mechanical means. It is convenient to have a name to designate the peculiar kind of attraction exerted between such particles. It has been called *chemism* or *chemical affinity.* The name, however, is only a name, and is used simply as a matter of convenience. Now, in all chemical phenomena, this peculiar kind of attraction is considered to be the cause. Just as the attraction of gravitation is said to be the cause of the motion of the heavenly bodies. The object of chemistry is the study of matter, so far as it is influenced by that kind of attraction which is called chemism.

In regard to the position which chemistry occupies among the sciences, it will be seen that it is primarily a branch of physics, if to the latter science is given its broadest scope. But, further, chemism always gives rise to the formation of new bodies, and the study of these in their relations to each other becomes a legitimate part of the object of chemistry. This allies the science to that branch of study embraced under the head Natural History. Owing to this twofold character, it is customary to treat the subject as forming an independent science, and, for many reasons, this is the most convenient method.

We have thus far recognized the existence of the force, chemism; and also become acquainted with one of the characteristics of its action. The knowledge of the force remained for a long time in this state, as the methods of investigation at first employed could not disclose its most important characteristics. Up to the latter part of the eighteenth century, the *qualitative* method of investigation

was of necessity the principal one employed in the study of chemical phenomena; that is to say, the quality of the substances allowed to act upon each other, and the quality of the product or products were noted, but little attention being given to the *amounts* of the substances employed, or of those obtained as products. As the importance of the *quantitative* method became more and more apparent, the means for applying it also gradually made their appearance. The balance, the *sine qua non* of chemistry, was improved, and, finally, in Lavoisier's hands led to tangible results. To its use is to be ascribed the correct explanation of the phenomenon of combustion, a phenomenon which, considered in all the varied forms in which it is presented to us, must be looked upon as the most important of all chemical phenomena. But, though the explanation of combustion was correctly given, no new property of chemism was discovered. A new example of the kind of action which was already known to characterize the force was added to the list; the key was given to a better understanding of the chemical nature of gaseous bodies; the indestructibility of matter became more distinctly evident than it had hitherto been; but the knowledge of chemism as such remained what it had been up to that time. That a definite result of great importance was obtained through a consideration of the quantitative relations of an experiment was the fact which, above all others, gave an impulse to the subsequent development of the science.

Investigations of chemical phenomena now took, in general, a different direction; and soon the united work of many hands succeeded in establishing a fundamental principle of the science. The first semblance of a general law governing chemical action made its appearance when it was finally established beyond a doubt that the combination of bodies, under the influence of chemism, always takes place in fixed proportions. This principle, though perhaps tacitly acknowledged by many chemists, was not fully established until the beginning of the present century. In 1803, a strong effort was made by Berthollet, in his work entitled *Statique chimique*, to prove the incorrectness of the principle, but the opposition called forth by this work, particularly from Proust, led to more and more careful examinations of the so-called chemical compounds, and thus to the firm establishment of the principle. Proust also showed

that two bodies can combine with each other in more than one proportion, and that for each combination the relative proportions of the constituents are fixed.

Dalton's Investigations.— In the year 1804, Dalton's investigations enabled him to take another advance-step. Another general law governing chemical action was discovered and propounded. This was the *law of multiple proportions.* As this is the foundation of the science, as it is at present, let us follow, somewhat in detail, Dalton's reasoning. Many substances had been analyzed before his time, and the percentages of the constituents had been determined with a fair degree of accuracy. He examined first two gases, both of which consist of carbon and hydrogen, viz., olefiant gas and marsh-gas. He analyzed them both, and determined the percentages of the constituents contained in them. These percentages are as follows:

Olefiant gas, 85.7 per cent. carbon, and 14.3 per cent. hydrogen.
Marsh-gas, 75.0 " " 25.0 " "

On comparing these numbers, he found that the ratio of carbon to hydrogen in olefiant gas is as 6 to 1; whereas, in marsh-gas it is as 3 to 1, or 6 to 2. The amount of hydrogen, combined with a given amount of carbon, is exactly twice as great in the one case as in the other.

For the two oxides of carbon, further, the following numbers were obtained:

Carbon monoxide, 42.86 p. c. carbon, and 57.14 p. c. oxygen.
Carbon-dioxide, 27.27 " 72.73 "

But 42.86 : 57.14 : : 6 : 8, and 27.27 : 72.73 : : 6 : 16. The amount of oxygen, combined with a given amount of carbon in carbon dioxide, is exactly twice as great as the amount of oxygen combined with the same amount of carbon in carbon monoxide. He saw, again, that, in olefiant gas, one part by weight of hydrogen combines with six parts by weight of carbon, and that, in carbon monoxide, eight parts by weight of oxygen combine also with six parts by weight of carbon. Water was now examined. It contains 88.89 per cent. oxygen and 11.11 per cent. hydrogen, and these numbers are to each other as 8 to 1. The numbers, which, in the first place, represent the combining proportions of oxygen and hydrogen respectively with carbon, are

also found to represent, in the second place, the combining proportions of oxygen and hydrogen with each other. Subsequent examinations of other compounds led to similar results, and thus Dalton had discovered the law of multiple proportions. This may be stated as follows:

> *If two bodies, A and B, form several compounds with each other, and we consider any fixed amount of A, then the different amounts of B, which combine with this fixed amount of A, bear a simple ratio to each other.*

This law has been fully confirmed by all investigations, which have been carried on since the time of Dalton. Thus, another characteristic of chemism was clearly pointed out.

Atomic Theory —But Dalton did not stop with the discovery of the law of multiple proportions; he sought for its explanation. He was thus led to propose the *atomic theory*, as affording the simplest explanation of the facts as observed.

The question as to the ultimate constitution of matter had frequently and from the earliest dates been discussed. Two views were held at different periods, and by different thinkers. According to one of these, matter was supposed to be indefinitely divisible; according to the other, it was supposed that there is a limit to the divisibility, and that this limit is reached when the division has been carried down to certain small particles called *atoms*. After the discovery of the law of multiple proportions, however, the atomic theory acquired a more definite form, as the existence of atoms was supposed to have a direct connection with chemical combinations. The results of Dalton's investigations are not fully stated in the law of multiple proportions as above given; another fact was made clear which is also of importance. The complete results may be stated as follows: It was shown that for each element a particular number might be selected, and that this number, or a simple multiple of it, would represent the proportion by weight in which this element combines with other elements. This is a fact, which involves no hypothesis regarding the nature of matter. The "combining numbers" of the elements may be used without any reference to or thought of the existence of atoms. But the question naturally suggests itself: Why do elements combine according to the laws of definite and multiple proportions? No absolute, final answer can be given to this question, but we can

imagine a cause, or, as it is commonly expressed, we can propose an hypothesis. This Dalton did. He supposed that chemical action takes place between atoms, *i. e.*, between particles that are indivisible and have definite weights. If chemical combination takes place between one atom of one substance and one atom of another substance, or between a simple number of atoms of one substance and a simple number of atoms of another, and these atoms have definite weights, then, indeed, the explanation of the laws of definite and multiple proportions is given.

Thus the idea of atoms became a much more tangible one than it had been up to that time. Not only were atoms supposed to have definite weights, but a method was given by means of which their relative weights could be determined. The number assigned to an element, representing its combining proportion, would also represent the relative weight of its atom. The fact that the combining proportion of an element was in some cases represented by a multiple of the simplest number was satisfactorily accounted for by supposing that in these cases more than one atom of the element combined with one of another element.

Determination of Atomic Weights.—The determination of combining numbers or atomic weights, as the figures were indiscriminately called by some, became now the chief, immediate problem of the science of chemistry. Dalton's atomic hypothesis was accepted by many, though not by all. The laws governing chemical combinations could not be doubted, but the explanation could be and was. Nevertheless the importance of determining for each element the characterizing number, call it atomic weight or combining proportion, was acknowledged by all; and consequently particular attention was given to this field of research during the period directly following the time of Dalton's publication. Let us see how thoroughly the desired object could be accomplished alone by the aid of the principles laid down by Dalton.

At the time of which we are speaking, the methods for chemical analysis were still far from perfect, and hence most of the determinations then made required subsequent corrections which were gradually made as analytical methods were improved. This fact, however, has nothing to do

with the subject under consideration. The principle alone is involved. The question to be answered is: Can we, on logical grounds, with the principles contained in Dalton's investigation, ever determine the relative weights of the atoms of elements? To decide this question we must first examine more carefully Dalton's method for determining atomic weights. In the following brief discussion, the correct numbers, as given by later analyses, are employed, instead of those originally found. This does not interfere with the principle, and does simplify the matter otherwise.

Method for the Determination of Atomic Weights dependent upon Analysis.—As the standard the combining number of hydrogen was first selected, and this made 1. Hydrogen combines with oxygen in the proportion of 1 : 8; and as water was the only known compound of hydrogen and oxygen, the conclusion was drawn that the two elements were united atom to atom, and hence the atomic weight of oxygen is 8. Further, nitrogen is combined with hydrogen in ammonia in the proportion of one part by weight of hydrogen to $4\frac{2}{3}$ parts by weight of nitrogen. Ammonia was the only compound of nitrogen and hydrogen known; and the same reasoning as that above employed, led to the conclusion that the atomic weight of nitrogen is $4\frac{2}{3}$. Considering for a moment these two simple cases, we see that the numbers thus found, as representing the relative weights of the atoms of oxygen and nitrogen, are founded partially upon hypothesis. There is nothing to decide as to the number of atoms of hydrogen or oxygen that are contained in water, nor of nitrogen and oxygen in ammonia, and, of course, as long as this number is unknown, it is impossible to draw any positive conclusion with reference to the atomic weights of nitrogen and oxygen. Any conclusion thus drawn is dependent upon a thorough knowledge of the compounds of the particular element under consideration. Such a number must finally be selected as is most in accordance with the facts. This selection must remain more or less arbitrary, as may be more clearly and decidedly shown.

Take again the case of oxygen. A second compound of hydrogen and oxygen is now known containing the elements in the proportion 1 : 16. At first sight, the explanation of this may appear simple enough. In this second compound there are two atoms of oxygen combined with

one of hydrogen, and thus the proportion is satisfied. But may we not with equal right decide that in water there are two atoms of hydrogen combined with one of oxygen? This would give us for oxygen the atomic weight 16, and, in the second compound, we would have contained one atom of each of the elements.

Further, if we attempt to determine the atomic weight of carbon by Dalton's method, we shall encounter difficulties fully as great, and our final selection among many numbers will be arbitrary. Taking olefiant gas, we have hydrogen combined with carbon in the proportion 1 : 6; in marsh-gas the proportion of the same constituents is 1 : 3 or 2 : 6. If we suppose that in olefiant gas the elements are combined atom with atom, then the atomic weight of carbon is 6, and consequently in marsh-gas we would have two atoms of hydrogen combined with one atom of carbon. But here again we can just as well suppose that in marsh-gas we have the simplest kind of combination, and this would give us for the atomic weight of carbon 3. Then in olefiant gas two atoms of carbon would be combined with one atom of hydrogen.

Finally, let us take the oxygen compounds of carbon. In carbon monoxide, carbon is combined with oxygen in the proportion of 6 : 8 or 3 : 4 whereas in carbon dioxide the corresponding proportion is 6 : 16 or 3 : 8. Now let us suppose the atomic weight of oxygen to be 8. Then, if carbon monoxide is the simpler of the two compounds, the atomic weight of carbon is 6; and in carbon dioxide there are two atoms of oxygen combined with each atom of carbon. Here, again, it is evident that we can just as well imagine carbon dioxide to be the simpler compound, in which case the atomic weight of carbon would be 3, and in carbon monoxide there would be two atoms of carbon combined with one atom of oxygen. Between these different possibilities it is impossible to draw a logical conclusion with the aid of the knowledge which can be obtained by analyses. The number of similar instances might be increased indefinitely; the inadequacy of the method could be made more strikingly clear by examples of a more complicated kind, but the cases mentioned are sufficient for our purpose; we must have other methods for the determination of atomic weights before we can get numbers which are not more or less arbitrary.

Equivalents.—This necessity was recognized first and most clearly by Wollaston in 1814. As no method presented itself to him which would furnish a firm foundation for the determination of atomic weights, he proposed to abandon the idea of atomic weights entirely, and to substitute for it that of the *equivalent*, thus, as he supposed, getting rid of all hypotheses and obtaining numbers that would be the simple expressions of proved facts. The equivalent of an element was to him that quantity of the element that possessed the same chemical value as a given quantity of another element, that quantity of an element that could play the same role as a given quantity of another element. According to the conditions of this definition, it is plain that, in order to know what portions of two elements are equivalent we must be able to compare the two. Hence, primarily, only of such elements as can be compared with each other, of such as possess a certain degree of similarity, can the equivalent quantities be determined. As this direct comparison is not always, nor, indeed, in the majority of cases, possible, recourse must be had to indirect comparison.

To illustrate this let us take an example. Hydrogen and chlorine combine with each other in the proportion of 1 part by weight of hydrogen to 35.5 parts by weight of chlorine, and from this fact we draw the conclusion that 35.5 parts of chlorine are equivalent to one part of hydrogen. We find in the same way that 8 parts of oxygen, 80 of bromine, 16 of sulphur, are all equivalent to 1 part of hydrogen. Knowing that 35.5 represents the equivalent of chlorine, we determine the quantities of sodium and silver that are respectively equivalent to this quantity of chlorine. We find for sodium 23 and for silver 108. These quantities of silver and sodium are further found to be equivalent to 8 parts of oxygen, 80 parts of bromine, and 16 parts of sulphur, and hence we conclude that they are also equivalent to one part of hydrogen. Thus the equivalents of sodium and silver have been determined by the method of indirect comparison. Sodium and silver do not combine with hydrogen, yet the equivalent numbers found are intended to express the proportions in which they would combine with hydrogen, providing such combination were possible. We are amply justified in this in most simple cases, but nevertheless it must be distinctly borne in mind

that such numbers as are determined by indirect comparison with the standard, whatever this may be, are not in the strictest sense expressions of proved facts; the last step in the determinations, however justified we may be in taking it, requires, nevertheless, the aid of hypothesis.

But if the difficulty thus referred to were the only one met with in the determination of equivalent numbers, such determinations would have nearly the full value claimed for them by Wollaston. This, however, is not the case. As soon as we consider any but the simplest compounds, we are left in fully as much doubt in regard to the equivalent numbers as we are in regard to atomic weights. If it be required to determine the quantity of carbon that is equivalent to 1 part of hydrogen, the compounds of the two elements must be examined. But there are a great many compounds of these two elements. Taking but two, olefiant gas and marsh-gas, we find that in the former (see *ante*, p. 16) 1 part of hydrogen is combined with (equivalent to) 6 parts of carbon; whereas, in the latter, 1 part of hydrogen is combined with (equivalent to) 3 parts of carbon. What shall here decide which is the correct number? It is evident from such instances as this that the idea of the equivalent is fully as uncertain as that of the atom was at the time we are considering. That an element could be equivalent to two entirely different quantities was in itself paradoxical if the original definition of equivalent was retained. These difficulties seem not to have been apparent to Wollaston. He continued his determinations of equivalents, and during this time a fusion of the ideas of equivalent and atomic weight took place unconsciously. As neither of these ideas was then definite, as to each of a number of elements, a number of atomic weights could be assigned, and almost as many equivalents, the succeeding period in the history of chemistry presents a disagreeably confused condition, until it became felt on all sides that some new idea or ideas must be introduced, if a firm foundation for the science was to be reached.

Determinations by Berzelius.—Before the necessary new ideas were introduced, the methods at hand were employed to the full extent. All known compounds of any given element were compared with each other, and a number finally selected, that would best satisfy the facts, to repre-

sent the equivalent of the element, or its atomic weight, as it was called by others. Berzelius attacked the subject most successfully. He laid down rules, by the aid of which, according to him, the number of atoms of an element contained in a compound could be determined, and hence also its atomic weight. Then, by more careful analyses than had been previously made, the atomic weights or equivalents of all the elements were determined. A large number of these determinations depended for their correctness upon chemical rules, similar to the following, given by Berzelius:

> *If an element forms several oxides, and the quantities of oxygen contained in them, as compared with a fixed quantity of the element, bear the proportion* 1 : 2, *then it is to be concluded that the first compound consists of one atom of the element and one atom of oxygen; the second, of one atom of the element and two atoms of oxygen (or two atoms of the element and four atoms of oxygen). If the proportion is* 2 : 3, *then the first compound consists of one atom of the element and two atoms of oxygen; the second, of one atom of the element and three atoms of oxygen, etc.*

This rule covers those cases in which it is required to determine the atomic weight of an element by a consideration of its oxides Other rules were given, in which sulphur compounds, etc., were made the basis of calculation.

It will be observed that, although in these rules the oxygen and sulphur are taken as the elements, the number of whose atoms varies, the other elements might theoretically be considered in the same way, and the atomic weights obtained would then be entirely different. An example will make this clear: Mercury combines with oxygen in two proportions. In the first compound, 8 parts of oxygen are combined with 200 parts of mercury; in the second, 16 parts of oxygen are combined with 200 parts of mercury. Adopting the rule above laid down, we would conclude that in the first compound, 1 atom of mercury is combined with 1 atom of oxygen, and, in the second, 1 atom of mercury with 2 atoms of oxygen. If, then, 8 is the atomic weight of oxygen, 200 is the atomic weight of mercury. But if, on the other hand, we consider the quantity of oxygen as remaining fixed, and that of the mercury as varying, then we would have in the first compound, 8 parts of oxygen com-

bined with 200 parts of mercury, and, in the second, 8 parts of oxygen combined with 100 parts of mercury; and, by a similar process of reasoning, we might draw the conclusion that the first compound contains 2 atoms of mercury to 1 atom of oxygen, and the second, 1 atom of mercury to 1 atom of oxygen; and thus we would obtain 100 as the atomic weight of mercury instead of 200, as found above. Berzelius had made certain observations on chemical bodies upon which he based his rules, but, as we shall see, these observations were not sufficient.

Another difficulty presented itself in the case of those elements that combine only in one proportion with oxygen. What should decide in regard to the number of atoms of oxygen contained in a compound of such an element? Here speculation was the only aid, and it often led to false results.

The Principle of Substitution employed in the Determination of Atomic Weights.—The researches of Berzelius added a large amount to the knowledge of the combining weights of the elements, and it must be acknowledged that the determinations made by him rested upon a firmer basis than the determinations made previously. He made the fullest and most logical use of purely chemical means, that could be made at the time. Subsequently, however, a new fact was discovered in connection with chemical compounds, which proved of great value in simplifying the consideration of chemical phenomena, and also aided materially in the solution of the problem of the determination of atomic weights. This is *substitution*. A brief explanation will suffice here for the purpose of exhibiting the connection of this subject with the problem with which we are at present dealing. It has been found that certain elements have the power of entering into compound bodies, driving out some of the constituents. For instance, water contains two atoms of hydrogen and one of oxygen; if we allow potassium to act upon water, a portion of the hydrogen is given off, and a new compound, containing both potassium and hydrogen, in addition to the oxygen, is the result. If now potassium be further allowed to act upon this new compound, the hydrogen contained in it is driven out, and potassium enters. Thus we obtain from water, by replacing its hydrogen by potassium, a compound containing two

atoms of potassium and one atom of oxygen. This kind of action is called *substitution.*

To show how, by taking into account the transformations included under this head, we may draw conclusions of importance with reference to atomic weights, one simple example will suffice: We have seen that the chief difficulty in determining atomic weights or equivalents by chemical means consists in the lack of data for estimating the number of atoms of an element contained in any given compound. Considering marsh-gas, we find that in it 1 part of hydrogen is combined with 3 parts of carbon, and, as above stated, we might conclude from this fact that the atomic weight of carbon is 3. If, however, we can by any means prove that the number of atoms of hydrogen contained in the gas, is greater than one, the conclusion would require modification. By means of the process of substitution, this can be proved, or at least it can be proved that the hydrogen contained in marsh-gas can be subdivided, and, hence, if we accept the atomic hypothesis, it follows that the compound contains in its smallest part more than one atom of hydrogen. By allowing chlorine to act upon marsh-gas under proper conditions, a portion of the hydrogen is replaced, and a compound containing hydrogen and chlorine is formed. This new compound treated with chlorine again gives up a portion of its hydrogen, and takes up chlorine in its place. This operation may be repeated four times, and thus finally a compound is obtained which contains only carbon and chlorine. Each time the same amount of hydrogen is given up, and is replaced by an equivalent amount of chlorine. Thus it is plain that the hydrogen originally contained in marsh-gas is divisible into four parts, and we are obliged to accept the conclusion that there are *at least* four atoms of hydrogen contained in marsh-gas —a conclusion which we could not possibly reach by the aid of the means heretofore considered. If now we take that amount of carbon which is in combination with four atoms of hydrogen as representing one atom (and, by a consideration of the whole list of carbon compounds, we are justified in this step), then the atomic weight of carbon is 12. The method, thus briefly illustrated, is capable of application to a considerable extent, but not to such an extent as to render it a general method for the determination of atomic weights.

Consideration of Chemical Decompositions for the purpose of determining Atomic Weights.—One more method of reasoning must be referred to as having been employed, either for the purpose of furnishing proofs of the correctness of atomic weights determined by other means, or for the direct determination of these weights. An example will best make this matter clear. We wish to know, for instance, how many atoms of hydrogen are combined with nitrogen in ammonia; or, having by the preceding method concluded that this number is 3, we wish to verify the conclusion by other observations. By treating nitric acid (which we will suppose to contain one atom of hydrogen to every atom of nitrogen) with hydrogen we obtain ammonia. Now, if we consider the amount of hydrogen that in nitric acid was in combination with the nitrogen, we find that, in the resulting ammonia, three times as much hydrogen is combined with the same amount of nitrogen. Further, ammonia combines directly with a number of compounds, and, if we examine the amount of hydrogen contained in this ammonia, we find that it must necessarily be represented with three or some multiple of three atoms of hydrogen. Thus, if we study the various cases in which ammonia is either formed, or destroyed, or enters into combination, we find always that the quantity of ammonia thus playing a part must contain three or some multiple of three atoms of hydrogen; and hence we are again led to the conclusion that, in ammonia at least three atoms of hydrogen are combined with every atom of nitrogen.

The methods we have thus briefly described comprise all we have at our command for the determination of atomic weights dependent upon purely chemical processes. Consider these methods as we may, we must see that they are inadequate to the accomplishment of their object. The determinations may indeed be made, but at last there must always remain a doubt concerning the result. If, then, we can approach the subject from an entirely different direction, we shall succeed in reducing this doubt to a minimum, if we find that the results at first obtained assert themselves as correct in the second instance. Before passing, however, to a consideration of new methods for making these determinations, it will be well to apply the knowledge we have

gained in fixing more definitely than has yet been done the ideas of elements and compounds.

Elements.—The theoretical idea of an element has already been stated. An element, strictly speaking, is a substance that cannot by any possible means be decomposed into kinds of matter that are unlike. This definition presupposes a knowledge of all possible means for decomposing bodies. Until we are positive that we are acquainted with all these means, we cannot be positive in regard to the existence of a single element. But it is plain that to assert the possession of this amount of knowledge would be in the highest degree presumptuous. We can then never assert positively that any given substance is an element; we can only say that, the means at our command being insufficient to bring about the decomposition of a given body, we consider this substance an element until such time shall arrive when, new means being given, it shall be shown to be compound. Numerous instances of the change of opinion concerning the elementary character of different substances might be adduced, prominent among which would be the alkaline metals, the oxides of which were for a time looked upon as elements; chlorine, which was looked upon as a compound body until it had been satisfactorily shown that we are not in possession of the means for decomposing it, etc., etc. Thus the number of elements, as stated at any given time, is entirely dependent upon the state of chemical analysis at that time, and is never an expression of an absolute fact. At present, the number of elements known is 66. In other words, we can recognize the existence of 66 different kinds of matter.

If we consider the atoms which make up an elementary substance, we see that they must necessarily be of the same kind, how far soever we consider the subdivision of the substance as taking place before the atom is reached. Accepting then the existence of atoms, an element may be defined as a substance made up of atoms of the same kind; and we shall see that the definition of an atom, which will be given further on, makes this definition of an element a strict one in every respect.

Compounds.—It has been stated that observation shows us the existence of at least two varieties of compound

bodies. To only one of these, however, is the name *compound* strictly applied, and then the name signifies a *chemical compound.* To the other class various names are applied, according to the nature of the substance, such for instance as *mechanical mixture, solution, alloy,* etc. At one time it was thought that no strict line of division could be drawn between these two classes. The same ultimate causes were supposed to give rise to the formation of both; and the constituents of both were supposed to be held together by the same agent. It may be shown that there is a marked difference between them, sufficient to enable us to say, in most cases, with which we have to deal.

1. If we examine chemical compounds, we find that one of their most prominent characteristics is the possession of properties which differ entirely from those of their constituents. Hydrogen, an inflammable gas, and oxygen, a gas and energetic supporter of combustion, combine to form a liquid, water, which is not inflammable and does not support combustion. Hydrochloric acid, a gas that turns vegetable blues red, and ammonia, a gas that turns vegetable reds blue, unite to form sal-ammoniac—a solid that is without influence upon vegetable colors. Chlorine, a gas, and mercury, a liquid, give a solid with none of the characteristic properties of either. The number of these examples might be increased indefinitely, and in each case a similar result would be reached.

2. It will be found that no purely mechanical means will suffice to separate the constituents of a chemical compound from each other; but for this purpose one of the so-called physical forces, as heat, light, electricity, chemism, is necessary.

3. The most important characteristic of chemical compounds is to be found in the proportion by weight in which the constituents are bound together. As regards any compound of two elements, it is a fact that the constituents are present in fixed proportions by weight. If we bring these elements together without reference to their quantities, and the proper conditions be brought about to induce combination, it is found that a definite quantity of one combines with a definite quantity of the other; and, if the quantity of either present is in excess of the fixed quantity necessary for the formation of the compound, this excess will remain in its original form after combination has taken place. We

can vary the proportions only to a very limited extent, and then not gradually, but according to a fixed rule. This is the fact which above all others enables us to assert positively that a given body is or is not a chemical compound.

Mechanical Mixtures.—To compare the second class of compounds with chemical compounds proper, let us first take the so-called mechanical mixtures. If we bring oxygen and nitrogen together, a homogeneous mixture of the two is formed, and this possesses the properties of both oxygen and nitrogen; such a mixture, for instance, is the atmosphere of the earth. Gases mix in this way by virtue of their inherent tendency to expand indefinitely and completely fill the space offered to them. It is, hence, unnecessary to suppose that any special force acts in this gas to hold the constituents together. Many solids may be mixed in various ways, but no matter how finely we may divide them, nor how intimately we may mix them, provided chemical combination does not take place, we can again separate the constituents of the mixture by mechanical means; and the mixture possesses all the original properties of its constituents. In both these cases, further, the most varied quantities of the substances may be employed, and, under the same conditions, the mixtures will be formed just as readily with one proportion as with another.

Solutions and Alloys.—On the other hand, those compounds, which are known under the names of solutions and alloys, are more closely allied to chemical compounds. We may have gases, liquids, or solids in the state of solution, that is, in combination with some liquid body, and to all appearance themselves in the liquid form. The external properties of one of the constituents are no longer recognizable, and they are, indeed, in part lost. A gas loses its ordinary elasticity when dissolved in a liquid. A solid loses the cohesion which before held its particles together. Two liquids combined in this way lose some of their original properties, and receive new ones that represent a mean between the lost ones. In all these instances the action between the particles of the dissolved bodies and the particles of the solvents is greater in its effect than the cohesion that originally held together the particles of the solid or liquid, or the repulsion that was exerted between the particles of the

gas. Further, we have the case of alloys or compounds of two or more metals. These alloys present the appearance of perfectly homogeneous bodies, but, nevertheless, possess most of the properties of the constituents. Here, too, the cohesion exerted between the particles of the original bodies is modified when the bodies are brought together.

On examining the above-mentioned cases more carefully, we find that there is, in almost all cases, a limit to the action. Substances that are soluble in water are not usually soluble to an unlimited extent; on the contrary, for any given temperature, the proportion of the substance that can be dissolved is fixed. But, between this fixed amount and the smallest possible quantity of the substance, all proportions are equally well dissolved. Some liquids mix with each other in all proportions, a perfectly homogeneous liquid being the result. Others dissolve each other to only a limited extent, the limits being, as in the case of solids and liquids, fixed for any given temperature.

Whatever the cause of the formation of these compounds in variable proportions may be, it is certain that the law or laws of its action have not been discovered up to the present. Some have looked upon it as identical with chemism, yet it appears that very distinct differences between the two can be pointed out.

The first feature of these compounds that indicates a radical difference in the two agents is the retaining of the chief original properties of the constituents. If we dissolve sodium chloride in water, we can obtain all the important effects from the solution that we could from the solid substance, and added to these we further obtain the effects of the water. And the same holds good for all solutions; they can produce the effects of the substances dissolved and of the solvent combined. As we have seen, this is not true of chemical compounds proper.

Again, the difference is specially marked, if we consider the proportions by weight in which the substances combine in the two cases. Whereas, whenever chemical compounds are formed, the constituents combine in fixed proportions,—in the case of mixtures, solutions, alloys, the constituents may combine in all possible proportions up to a certain fixed limit.

Whether it would be expedient, then, to consider chemism and the cause of the formation of solutions, etc., as iden-

tical, but differing in degree, is a question that cannot be here discussed. Certain it is, from the above remarks, that there exists sufficient difference between them to warrant us, for the present, in restricting the use of the name chemism to the designation of that force which is the essential cause of the formation of chemical compounds. In this sense it will be used in the following pages. The atomic theory accounts for the fact that bodies combine in definite proportions, by supposing them to combine atom to atom, and these atoms to possess definite weights. According to this, chemism, in its restricted sense, is the force which is exerted between atoms. It will be shown that these atoms may be either like or unlike. If they are like, the resulting body is an element; if they are unlike, the resulting body is a chemical compound.

It is plain, from the foregoing, that chemical compounds and elements are the only substances, the study of which can lead to definite conclusions concerning the action of chemism, and hence we must confine ourselves to these in our subsequent study of this force. And, first, we must return to that fundamental problem of chemistry—the determination of atomic weights. It having been shown that results, reached by the methods already given, must necessarily be uncertain, we now proceed to attack the subject from a wholly new side.

II.

EXAMINATION OF GASEOUS ELEMENTS AND COMPOUNDS.

As bodies present themselves to us in three different states of aggregation, the solid, liquid, and gaseous, so our methods of investigation of bodies must take different directions. Gases possess certain properties, which solids and liquids do not possess, and in solids and liquids we detect certain general properties that we cannot detect in gases. The study of bodies in the form of gas or vapor has led to very important results of lasting influence upon the science, and to these let us direct our attention.

Investigations of Gay Lussac.—In the year 1808, Gay Lussac and Humboldt discovered the fact that when hydrogen and oxygen combined to form water, the combination takes place between 2 volumes of hydrogen and 1 volume of oxygen. The simplicity of this relation induced Gay Lussac to take up the study of other gaseous bodies, with the view of determining whether similar relations exist between the volumes of other combining gases. His research enabled him soon after to deduce the following law of combination by volumes:

> *When two or more gaseous substances combine to form a gaseous compound, the volumes* of the individual constituents as well as their sum bear a simple relation to the volume of the compound.*

Thus, when hydrogen and chlorine unite to form hydrochloric acid, it was found that 1 volume of hydrogen and 1 volume of chlorine form 2 volumes of hydrochloric acid gas. Two volumes of hydrogen and 1 volume of oxygen

* In all cases, where the volumes of different gases are compared, the gases are, of course, supposed to be under the same conditions of pressure and temperature.

give 2 volumes of water-vapor; 2 volumes of nitrogen and 1 volume of oxygen give 2 volumes of nitrous oxide. Further, 3 volumes of hydrogen and 1 volume of nitrogen give 2 volumes of ammonia, etc.

On comparing this result with that already obtained by Dalton, and making use of the atomic hypothesis, according to which combination between elements takes place between their atoms, we see that some simple relation must exist between the volumes of gases and the relative number of atoms contained in these volumes. This we may express in general terms as follows:

> *The number of atoms contained in a given volume of a gaseous body bears a simple relation to the number of atoms contained in the same volume of other gaseous bodies.*

As will be readily seen, this gives no foundation for the determination of atomic weights, inasmuch as we have no means of fixing the value of the "simple ratio," and without this we cannot determine the relative number of atoms contained in a given volume of gas. We know that two volumes of hydrogen combine with 1 volume of oxygen, and we know that 2 parts by weight of hydrogen combine with 16 parts by weight of oxygen. Further, the atomic hypothesis tells us that a certain number of atoms of hydrogen of fixed weight combine with a certain number of atoms of oxygen of fixed weight, and that these numbers bear a simple relation to each other; hence, the relation between the number of atoms of hydrogen in the 2 volumes and the number of atoms of oxygen in the 1 volume, must be a simple one, but the facts do not furnish us with sufficient data to enable us to state what this relation is; without further aid, either from new facts or speculations, we cannot say what the atomic weights of these elements are.

Avogadro's Speculations.—The numbers expressing the specific gravities of gases or vapors are those numbers which express the relative weights of equal volumes of these gases or vapors. Hence, it is but re-stating, in another form, the principle above laid down, to say that the specific gravities of gaseous bodies bear a simple relation to the atomic weights of these bodies. The force of this statement will be readily recognized on comparing the specific gravities of some gases with the atomic weights of the same bodies de-

termined by chemical means. The atomic weights, as determined by chemical means, however, differed from each other according to the method employed in this determination; but the difference being that between one number and some multiple of that number, it is immaterial which of these numbers we employ for the purposes of the comparison. Let us, then, take the first of those determined. The following table hardly needs explanation. The numbers in the second column (d) represent the specific gravities of the elements in the form of gas or vapor; the fourth column contains the ratios between the atomic weights (A) and $d = \frac{A}{d}$.

Element.	d.	A.	$\frac{A}{d}$.
Hydrogen, ...	0.0692	1	14.45
Chlorine, ...	2.440	35.5	14.55
Bromine, ...	5.54	80	14.44
Iodine, ...	8.716	127	14.57
Oxygen, ...	1.10563	8	7.24
Sulphur, ...	2.23	16	7.17
Selenium, ...	5.68	39.7	6.99
Tellurium, ...	9.08	64	7.05
Nitrogen, ...	0.9713	14	14.41
Phosphorus, . . .	4.50	31	6.89
Arsenic	10.6	75	7.08
Mercury, ...	7.03	100	14.22
Cadmium, ...	3.94	56	14.21

We see thus that the relation between the specific gravity and the atomic weight of seven of these thirteen elements is the same, being expressed by a number varying but little from 14.4. In the cases of the six remaining elements of the list the relation is, also, virtually the same, about 7.1. And, in the latter case, the ratio is expressed by a number half as great as the first.

A consideration of these relations led Avogadro,* in 1811, to propose an hypothesis, which, if it is well founded, must prove of the greatest service in simplifying the problem of determining the atomic weights—at least of gaseous

* In 1814 Ampère proposed a similar hypothesis.

bodies. It will be seen that, if in the above schedule the atomic weights of oxygen, sulphur, selenium, tellurium, phophorus and arsenic be doubled, the ratio $\frac{A}{d}$ for all the elements in the list will be the same constant number, viz., about 14.4. But the atomic weights above given have been determined purely empirically, and we are as much justified in considering these numbers doubled as the true atomic weights, as we are in accepting the ones given. If we make this change, then, for the above thirteen elements, the following statement will be true: The atomic weights are to each other as the specific gravities of the vapors. An examination of compound gaseous bodies showed further that a simple relation also exists between their specific gravities and the numbers expressing the sum of the atomic weights of the constituents, these sums being to each other as the specific gravities. Avogadro's hypothesis to account for these relations may be stated in the following words:

> *All gases or vapors, without exception, contain, in the same volume, the same number of ultimate particles or molecules.*

The molecules were not considered to be identical with the atoms, and it is well here to draw the distinction between the two as clearly as possible. Molecules of compounds, as understood by Avogadro, and as understood at present, are the theoretically smallest particles of these compounds. The molecule of water is the smallest particle of water that can exist as water. As water, however, is composed of two elements, of course, the smallest particle of water must necessarily still be divisible into these constituents. The component parts of molecules are called atoms, and these are indivisible. In the case of water, the molecule has the same composition as the mass of the compound, but, as will be shown, this molecule of water consists of two atoms of hydrogen and one atom of oxygen. The atoms are held together by chemism, the molecules by cohesion.

Now, there are good reasons, which will be considered below, for believing that, in their internal structure, elementary substances are, in some repects, analogous to compounds, and this belief was made a fundamental condition of Avogadro's hypothesis. According to this, it is impossible by purely mechanical means to subdivide an element so far as to reach its atoms; but, if we suppose it divided as far as

possible by such means, we reach, as in the case of compounds, the molecule of the element, which is the smallest particle of the element that can exist and play the part of the element. This molecule, however, usually consists of atoms, which are held together by chemism, and can hence be separated only by means, other than mechanical, that have the power of overcoming the force.

From these considerations we are enabled to give definitions of the terms *atom* and *molecule:*

A molecule is the smallest particle of a compound or element that is capable of existence in a free state. A breaking up of the molecule necessitates the destruction of the properties of the compound, and almost always of those of the element.

Atoms are the indivisible constituents of molecules. They are the smallest particles of elements that can take part in chemical reactions, and are, for the greater part, incapable of existence in the free state, but are always found in combination with other atoms, either of the same kind or of different kinds.

And now the justice of the definitions of elements and compounds given above (see pp. 27, 28) will be recognized; viz., an element is a substance made up of atoms of the same kind; a compound is a substance made up of atoms of unlike kind.

Recognizing thus fully the distinction between atoms and molecules, we are prepared to further follow the reasoning of Avogadro.

The experiments of Gay Lussac had already proved that under the influence of heat, all gases expand in the same proportion for the same increase of temperature, and diminish in volume to the same extent for the same decrease of temperature. Further, Mariotte, in France, and Boyle, in England, had shown that all gases conduct themselves in the same way under the influence of increased or decreased pressure; that for the same increase or decrease of pressure the consequent decrease or increase of volume is for the same volume of all gases the same. These facts considered independently would lead to a suspicion that all gases possess a similar internal structure, and the simplest hypothesis to account for this is just the hypothesis of Avogadro—that the same volumes of all gaseous bodies contain the same number of molecules. This subject has been con-

sidered exhaustively from a purely physical standpoint. The principles of the mechanical theory of gases being accepted, it has been shown that the hypothesis of Avogadro logically follows; and then, by a purely mathematical process of reasoning, it has been shown that the hypothesis is an absolute necessity. A discussion of the subject in the direction indicated cannot be taken up here.

As a grand result of the investigations that have been made on the internal structure of gases, it may be stated that Avogadro's hypothesis has throughout asserted its correctness, and it has at last become of fundamental importance in the science of chemistry. It is at present almost universally accepted by chemists, some, indeed, going so far as to speak of it as a *law*.

Determination of Molecular Weights.—What, then, do we gain by accepting the hypothesis? It is plain that if equal volumes of all gases contain the same number of molecules we have a means given us at once for ascertaining the relative weights of these molecules. We have merely to determine the relative weights of equal volumes of the gases, and the numbers obtained will bear the same relations to each other as the molecular weights. Then accepting the weight of some molecule as a standard, and expressing the weights of the others in terms of this standard, the molecular weights are determined. Let us, for example, take hydrochloric acid as the standard molecule. As this compound contains 35.5 parts by weight of chlorine to 1 of hydrogen, the smallest figure which we can take to represent its molecular weight, without representing the weight of hydrogen by a figure less than 1, is 36.5. We accordingly accept this as the molecular weight of hydrochloric acid. We now determine the specific gravity of the gas, and express the result in terms of air. The figure is 1.247, or, to be explicit, if the weight of a given volume of air be represented by 1, then the weight of the same volume of hydrochloric acid gas is represented by 1.247. As, according to Avogadro's hypothesis, the molecular weights of gaseous bodies bear the same relation to each other, as their specific gravities, it is only necessary to determine in one particular case what relation exists between the molecular weight and the specific gravity. The molecular weight accepted for hydrochloric acid, for the reasons above given, is 36.5, the spe-

cific gravity, determined by actually weighing the gas, is 1.274. The relation between the two figures, is expressed thus, $\frac{3.65}{1.274} = 28.65$; or, calling the specific gravity d, and the molecular weight M, we have for hydrochloric acid $\frac{M}{d} = 28.65$, $M = d \times 28.65$. Having determined the relation between the specific gravity and molecular weight of one gaseous body, we have, however, determined it for all, and we thus have in our possession a method for determining molecular weights which depends upon the determination of the specific gravities of gases or vapors. If the rule is perfect, and the figures obtained by experiment were absolutely accurate, then by dividing the molecular weight of any gaseous body by its specific gravity, we should in every case obtain the same quotient. Owing partly to the imperfection of the methods for determining specific gravities and for analyzing chemical compounds, the figures actually obtained do not give exactly the quotient obtained in the case of hydrochloric acid. The average of the results is more nearly 28.88, and, as this is the figure obtained by dividing the molecular weight of hydrogen by the specific gravity, it is the one commonly given in stating the rule. Instead of being $M = d \times 28.65$, it is $M = d \times 28.88$.

Applying the rule to the determination of molecular weights, we obtain results which approximate the truth, and which enable us to decide whether the molecular weight is a certain figure or a multiple of this figure. Chemical analysis then comes in and tells us exactly what the number is. To illustrate this, take the case of water. We find by determining the specific gravity of water vapor and multiplying by 28.88 that the molecular weight is 17.99. This enables us at once to decide between the various possibilities, 9, 18, 27, etc. If we now determine with great accuracy the proportions by weight in which hydrogen and oxygen are combined with each other in water, we shall be able to state exactly what the molecular weight of water is. According to the most reliable investigations the figure is 17.96. The coincidence of the numbers determined according to the two methods in the case of a few elements and compounds will be seen in an examination of the subjoined table. The numbers under M are those found by the analytical method, that one of a series of multiples being selected that agrees

most nearly with the number found according to the rule $M = 28.88 \times d$.

Name.	Specific gr. $= d$.	$28.88 \times d$.	M.
Hydrogen,	0.06926	2	2
Nitrogen,	0.9713	28.05	28
Oxygen,	1.10563	31.93	32
Sulphur,	2 23	64.4	64
Chlorine,	2.45	70.75	71
Cadmium,	3.94	113.78	112
Phosphorus,	4.35	125.62	124
Bromine,	5.54	159.99	160
Selenium,	5.68	164.03	158.8
Mercury,	6.98	201.58	200
Water,	0.623	17.99	18
Hydrochloric acid,	1.247	36.11	36.5
Sulphur dioxide,	2.247	64.89	64
Ammonia,	0.597	17.24	17
Phosphorus trichloride,	4.88	140.93	137.5
Arsenic trichloride,	6.30	181.94	181.5
Boron chloride,	3.942	113.84	117.5
Marsh-gas,	0.557	16.08	16
Methyl chloride,	1.736	50.13	50.5
Chloroform,	4.20	121.29	119.5
Tin chloride,	9.20	265.69	260
Silicon chloride,	5 94	171.55	170
Zinc-methyl,	3.29	95.02	95.2
Aluminium chloride,	9.35	270.03	267
Iron trichloride,	11.39	328.94	325

Number of Atoms in the Molecules of Elements.—Although we are thus enabled to determine by a simple process the molecular weights of those elements which are gases under ordinary conditions, or which can be converted into gases, an important part of the problem—the determination of the atomic weights—yet remains to be solved. If we knew in each case how many atoms are contained in a molecule, our difficulties would be at an end; but this we plainly do not know without the introduction of considerations of a different kind from those with which we have had to deal thus far. Taking hydrochloric acid as the standard in determining the molecular weights, and representing its molecular weight by 36.5, because that is the smallest figure permissible, if the amount of hydrogen in it is not to be expressed by a figure less than 1, we find that the molecular weight of hydrogen, determined by the

rule of Avogadro, is 2. Now the part of hydrogen contained in hydrochloric acid, which is represented by 1, must be at least an atom of hydrogen. Or, further, the 36.5 parts of hydrochloric acid, representing the molecule, must be made up of at least one atom of hydrogen, weighing one part, and one atom of chlorine, weighing thirty-five and five-tenths parts. But, as we find that the molecule of hydrogen weighs two parts, it follows that the molecule must be at least twice as heavy as the atom, or the molecule must contain at least two atoms. Avogadro reasoned as follows, with reference to some of the simple chemical compounds: Given hydrochloric acid, it is required to know how many atoms are contained in a molecule of hydrogen and in a molecule of chlorine. If in a certain volume of hydrogen there are contained say 100 molecules, then in the same volume of chlorine there is contained the same number of molecules. Now it is known that 1 volume of hydrogen combines with 1 volume of chlorine. Two volumes of hydrochloric acid gas are formed, and, according to the hypothesis, these two volumes in the case under consideration contain 200 molecules. But each molecule of hydrochloric acid must contain at least one atom of chlorine; hence, in 100 molecules of hydrogen and 100 molecules of chlorine there must be contained at least 200 atoms of chlorine and 200 atoms of hydrogen, or a molecule of either hydrogen or chlorine must contain at least two atoms. Further, as no simpler compound of hydrogen or of chlorine is known than hydrochloric acid, any conclusions which we may draw from a consideration of this compound must be valid for all compounds of these elements. The supposition that two atoms form the molecule of hydrogen and of chlorine satisfies all the facts known to us, and we hence rest with this supposition. It must, however, be distinctly borne in mind that no proof is here given of the absolute number of atoms contained in the molecules of hydrogen and chlorine. We can only say that *at least* 2 atoms must be present in each of the molecules. There may be a much greater number, but the data permit no speculations beyond this number 2.

For all similar cases a similar process of reasoning may be employed, and with the same results. Whenever 1 volume of an elementary gas or vapor combines with 1 volume of another elementary gas or vapor to form 2 volumes of a

compound gas or vapor, we are justified in concluding that each molecule of these elements contains two atoms. The elements that come under this head are hydrogen, chlorine, bromine, and iodine.

If we pass to oxygen, we find a material difference in the method of combination. Here 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of water-vapor. Let us reason as above. If in 1 volume of oxygen there are contained 100 molecules, then in 2 volumes of hydrogen there are 200 molecules. These 300 molecules combine to form 200 molecules of the compound. Now, in the molecule of water, there must be contained at least 1 atom of oxygen and 1 atom of hydrogen; hence, there must be at least 200 atoms of oxygen and 200 atoms of hydrogen. But we know that in the original 200 molecules of hydrogen there were contained 400 atoms; hence, in each molecule of water, there must be 2 atoms of hydrogen. Water is the simplest compound of oxygen known to us (*i. e.*, it contains the smallest quantity of oxygen in the molecule), and on this account we suppose the molecule of water to contain 1 atom of oxygen. If, then, each water molecule contains 2 atoms of hydrogen and 1 atom of oxygen, in the 200 molecules of water there are 200 atoms of oxygen and 400 atoms of hydrogen, and these are obtained from 100 molecules of oxygen and 200 molecules of hydrogen. Therefore, each molecule of oxygen, as well as each molecule of hydrogen, contains 2 atoms. For sulphur the same is true, and is proved in a similar manner.

Another method of reasoning, starting from entirely different facts, also led Favre and Silbermann to suggest that the molecule of oxygen consists of 2 atoms. They proved that carbon, when burned in protoxide of nitrogen, evolves more heat than when burned in oxygen. The most natural interpretation of this fact is given in assuming that, in each experiment, a chemical combination is destroyed while another is formed; and that the amount of heat actually evolved is the difference between the amount of heat disengaged by the union of carbon with oxygen and the amount of heat absorbed by the decomposition of the oxide of oxygen in the first instance, and of oxide of nitrogen in the second. And, if the thermic effect is less with oxygen than with protoxide of nitrogen, that is due to the circumstance that oxide of oxygen (the molecule of oxygen

O = O) absorbs more heat in decomposing than does the molecule of protoxide of nitrogen.

One volume of nitrogen combines with 3 volumes of hydrogen to form 2 volumes of ammonia. Hence in the molecule of ammonia there are 3 atoms of hydrogen, and, ammonia being the simplest compound of nitrogen, we suppose that these 3 atoms of hydrogen are combined with 1 atom of nitrogen. As each molecule of ammonia contains 1 atom of nitrogen, and as, further, there are formed twice as many molecules of ammonia as there were molecules of nitrogen originally, it follows that the molecule of nitrogen contains at least 2 atoms.

By this means we are enabled to determine the atomic weight of the elements mentioned, for, if in their molecules 2 atoms are contained, we have only to divide the molecular weight—found by Avogadro's rule, and corrected by analytical methods—by two. But, accepting the atomic weights of hydrogen, chlorine, bromine, and iodine as known, we are enabled by another process to determine the atomic weights of such elements as combine with these to form gaseous compounds.

Take again water. We find by a comparison of the compounds of oxygen that the molecule of water, as stated above, contains the smallest quantity of this element; and hence we suppose this quantity to represent 1 atom. We first find the molecular weight from the specific gravity of the vapor. This is 18. We analyze the compound, and find that it contains 88.89 per cent. oxygen, and 11.11 per cent. hydrogen, or 8 parts of oxygen to 1 part of hydrogen. This being the relative proportion of the two elements in the compound, in 18 parts by weight, which represent the molecule, there are contained 16 parts of oxygen and 2 parts of hydrogen. The atomic weight of oxygen is hence 16, and in water 1 atom of oxygen is combined with 2 atoms of hydrogen. In a similar way, on comparing the molecular weights of the compounds of nitrogen we find that the amount of this element contained in the molecule of ammonia is as small as in any other. The molecular weight of ammonia we find to be 17. The analysis shows us that the elements are combined in the proportion of 14 parts by weight of nitrogen to 3 parts by weight of hydrogen. Hence 14 is the atomic weight of nitrogen, and the mole-

cule of ammonia contains 1 atom of nitrogen and 3 atoms of hydrogen.

Molecules of Elements which contain more or less than two Atoms.—The molecules of the elements considered contain each at least 2 atoms. This, however, is not true of the molecules of all elements.

Among those compounds of phosphorus which may be looked upon as containing 1 atom of this element in the molecule is phosphine. The molecular weight of phosphine is 34. The elements are contained in it in the proportion of 31 parts of phosphorus to 3 parts of hydrogen. Hence 31 is the atomic weight of phosphorus. On the other hand, we find the molecular weight of phosphorus itself to be 124, which shows that at least 4 atoms are contained in the molecule. The same is true of arsenic.

For reasons similar to those given above, the molecule of mercuric chloride is supposed to contain one atom of mercury. The molecular weight of this compound is found to be 270.5, and the elements are contained in it in the proportion of 200 parts of mercury to 71 parts of chlorine, which gives 200 as the atomic weight of mercury, and the atom of this element is combined with two atoms of chlorine. The molecular weight of mercury is 200; hence, in the molecule of mercury there is contained but one atom. The same coincidence of atomic and molecular weight is noticed in the case of cadmium.

Kundt and Warburg have described an interesting experiment, the results of which also show that the molecule of mercury in all probability consists of a single atom. The quantity of heat contained in a gas is defined as the total energy of its molecules, and this energy consists solely in progressive motion, if the molecule is looked upon as a mere material point. According to this, it is a simple matter to calculate the relation between the specific heat of a gas at constant volume and the specific heat at constant pressure. It was found, however, that, in the case of the gases examined, the theoretical value of this relation is larger than the value actually obtained by observation. If c represents the specific heat at constant volume, and c' the specific heat at constant pressure, then $\frac{c'}{c} = k$ represents the relation above referred to. According to the theory, $k =$

1.67, whereas observation gives $k = 1.405$. In other words, it requires more heat to raise the temperature of a gas, the volume remaining unchanged, than the theory demands. The heat, which thus disappears, may be transformed into an inter-molecular motion, *i. e.*, the atoms, composing the molecule, may have a motion relative to some centre of gravity. This motion would not show itself as temperature. If the molecule of the gas consists of one atom, then the theoretical and observed value of k should be identical. The examination of mercury gave for k the value 1.67, which is that above given as the result of calculation. It is thus shown, by a method entirely independent of chemistry, that the molecule of mercury conducts itself like a material point, and this could only be the case, if it consisted of one atom.

Varying Number of Atoms in the Molecule of one and the same Element.—The specific gravity of the vapor of sulphur was stated in the above table (p. 39) to be 2.23, and this leads to the molecular weight, 64. Now, it has been found that the specific gravity of this vapor varies according to the temperature at which it is determined. The determinations, which gave the number 2.23, were made at temperatures above 800° C. (860° and 1040°). Other determinations, however, made below 800° gave different results. At 524° (Dumas) and 508° (Mitscherlich) the specific gravity was found to be 6.62 and 6.90 respectively, or three times as great as at the higher temperatures. These latter determinations give the molecular weight 192, and, if 32 be the atomic weight of sulphur, then in the molecule of the vapor below 800° there are contained 6 atoms, whereas above 800° there are contained only 2 atoms in the molecule. Selenium, so similar to sulphur in all other respects, presents similar phenomena, though not in so marked a degree. Here, too, it is noticed that the specific gravity of the vapor decreases with an increase of temperature, or, what is the same thing, according to Avogadro's hypothesis, the molecular weight decreases with an increase of temperature.

Analogous results have been obtained with iodine, and these are of special interest, as they seem to indicate the possibility of proving that the molecule of iodine consists of 2 atoms, and no more. The normal specific gravity of iodine vapor is 8.8, corresponding to the molecular weight,

254. It was first shown by Victor Meyer that at 1027° C. the specific gravity is reduced to 5.8. At 1468° J. M. Crafts and F. Meier showed that it is still further reduced, becoming 5.1. Victor Meyer then succeeded in reducing it to 4.5 by heating to a higher temperature; and, finally, Crafts and Meier proved that by a further elevation of temperature the specific gravity is not reduced below the value 4.5, which is very nearly one-half the normal. The simplest interpretation of these phenomena is this: Under ordinary conditions, the molecule of the vapor of iodine consists of 2 atoms. When the temperature is elevated, there is a gradual decomposition of the molecules into 2 atoms each. This decomposition continues, as the temperature is raised, until finally all the molecules are transformed into atoms. When this limit is reached, no further decomposition being possible, the specific gravity remains unchanged, even though the temperature be raised still higher. The fact that the reduction in the specific gravity stops when it reaches half the normal is especially significant, as it furnishes strong evidence of the presence of 2, and only 2, atoms in the molecule of iodine.

The application of the method thus described for the determination of the molecular weights of elementary bodies is limited, as we can convert only a few of these bodies into vapor. Of many elements, however, we know compounds that are capable of conversion into vapor, or are themselves gaseous, and, as we can determine the molecular weights of these compounds, we are thus enabled to determine the atomic weights. The following table contains a number of such compounds, together with the specific gravities (d); the products of the densities into the constant 28.88 ($d \times 28.88$); the molecular weights as found by analytical methods (M); and, finally, the relative quantities of the constituents of the compounds contained in the molecules as determined by analysis:

Name.	*d.*	$d \times 28.88$	*M.*	Constituents.
Aluminic chloride, .	9.35	270	267.6	54.6 parts aluminium.
				213 " chlorine.
Aluminic bromide, .	18.6	537.2	534.6	54.6 " aluminium.
				480 " bromine.
Aluminic iodide, .	27	780	816.6	54.6 " aluminium.
				762 " iodine.
Antimonous chloride,	7.8	225.3	228.5	122 " antimony.
				106.5 " chlorine.
Triethylstibine, .	7.44	214.8	209	122 " antimony.
				72 " carbon.
				15 " hydrogen.
Antimony trioxide, .	19.79	571.5	576	480 " antimony.
				96 " oxygen.
Arsenous iodide, .	16.1	464.9	456	75 " arsenic.
				381 " iodine.
Arsine, . . .	2.7	77.97	78	75 " arsenic.
				3 " hydrogen.
Arsenic trichloride, .	6.3	181.9	181.5	75 " arsenic.
				106.5 " chlorine.
Arsenic trioxide, .	13.79	398.3	396	300 " arsenic.
				96 " oxygen.
Cacodyl chloride, .	4.56	131.7	140.5	75 " arsenic.
				35.5 " chlorine.
				24 " carbon.
				6 " hydrogen.
Cacodyl cyanide, .	4.65	134.3	131	75 " arsenic.
				14 " nitrogen.
				36 " carbon.
				6 " hydrogen.
Bismuthous chloride,	11.35	327.8	316.5	210 " bismuth.
				106.5 " chlorine.
Boric chloride, .	3.942	113.8	117.5	11 " boron.
				106.5 " chlorine.
Boric fluoride, . .	2.312	66.8	68	11 " boron.
				57 " fluorine.
Boric bromide, . .	8.78	253.5	251	11 " boron.
				240 " bromine.
Trimethylborine, .	1.93	55.7	56	11 " boron.
				36 " carbon.
				9 " hydrogen.
Cadmium bromide, .	9.25	267.1	271.8	111.8 " cadmium.
				160 " bromine.
Marsh-gas, . .	0.557	16.1	16	12 " carbon.
				4 " hydrogen.
Methyl fluoride, .	1.186	34.3	34	12 " carbon.
				3 " hydrogen.
				19 " fluorine.

Name.	*d.*	$d \times 28.88$	*M.*	Constituents.
Methyl chloride, .	1.731	50	50.5	12 parts carbon.
				3 " hydrogen.
				35.5 " chlorine.
Methyl bromide, .	3.253	93.9	95	12 " carbon.
				3 " hydrogen.
				80 " bromine.
Methyl iodide, . .	4.883	141	142	12 " carbon.
				3 " hydrogen.
				127 " iodine.
Methyl nitrate, .	2.64	76.2	77	12 " carbon.
				3 " hydrogen.
				14 " nitrogen.
				48 " oxygen.
Methyl alcohol, .	1.12	32.3	32	12 " carbon.
				4 " hydrogen.
				16 " oxygen.
Carbon monoxide, .	0.968	27.96	28	12 " carbon.
				16 " oxygen.
Carbon dioxide, .	1.529	44.16	44	12 " carbon.
				32 " oxygen.
Chloroform, . .	4.2	121.3	119.5	12 " carbon.
				1 part hydrogen.
				106.5 parts chlorine.
Carbon tetrachloride,	5.24	151.3	154	12 " carbon.
				142 " chlorine.
Carbon oxichloride, .	3.505	101.2	99	12 " carbon.
				16 " oxygen.
				71 " chlorine.
Carbon oxisulphide, .	2.105	60.8	60	12 " carbon.
				16 " oxygen.
				32 " sulphur.
Carbon sulphide, .	2.645	76.39	76	12 " carbon.
				64 " sulphur.
Hydrocyanic acid, .	0.948	27.4	27	12 " carbon.
				14 " nitrogen.
				1 part hydrogen.
Cyanogen chloride, .	2.13	61.5	61.5	12 parts carbon.
				14 " nitrogen.
				35.5 " chlorine.
Cyanic acid, . .	1.5	43.3	43	12 " carbon.
				14 " nitrogen.
				16 " oxygen.
				1 part hydrogen.
Hydrochloric acid, .	1.247	36	36.5	35.5 parts chlorine.
				1 part hydrogen.
Chromic acichloride,	5.55	160.3	155	52 parts chromium.
				32 " oxygen.
				71 " chlorine.

Name.	*d.*	$d \times 28.88$	*M.*	Constituents.
Cuprous chloride, .	6.93	200.1	197.4	126.4 parts copper.
				71 " chlorine.
Indium chloride, .	7.87	227.3	219.9	113.4 " indium.
				106.5 " chlorine.
Hydriodic acid, .	4.443	128.3	128	127 " iodine.
				1 part hydrogen.
Ferric chloride, .	11.07	320	325	112 parts iron.
				213 " chlorine.
Lead chloride, .	9.5	274.4	278	207 " lead.
				71 " chlorine.
Lead methyl, . .	9.6	277.2	267	207 " lead.
				48 " carbon.
				12 " hydrogen.
Mercuric chloride, .	9.8	283	271	200 " mercury.
				71 " chlorine.
Mercuric bromide, .	12.16	351.2	360	200 " mercury.
				160 " bromine.
Mercuric iodide, .	16.2	468	454	200 " mercury.
				254 " iodine.
Mercury methyl, .	8.29	239.4	230	200 " mercury.
				24 " carbon.
				6 " hydrogen.
Mercury ethyl, . .	9.97	287.9	258	200 " mercury.
				48 " carbon.
				10 " hydrogen.
Molybdic chloride, .	9.46	273	269.5	92 " molybdenum.
				177.5 " chlorine.
Niobic chloride, .	9.6	277.2	272.5	95 " niobium.
				177.5 " chlorine.
Niobic acichloride, .	7.88	227.6	217.5	95 " niobium.
				16 " oxygen.
				106.5 " chlorine.
Ammonia, . .	0.597	17.2	17	14 " nitrogen.
				3 " hydrogen.
Nitric oxide, . .	1.039	30	30	14 " nitrogen.
				16 " oxygen.
Nitrous oxide, . .	1.520	43.9	44	28 " nitrogen.
				16 " oxygen.
Osmium tetroxide, .	8.89	256.7	263	199 " osmium.
				64 " oxygen.
Water, . . .	0.623	17.99	18	16 " oxygen.
				2 " hydrogen.
Phosphine, . .	1.18	34.1	34	31 " phosphorus.
				3 " hydrogen.
Phosphorus trichloride, . . .	4.85	140	137.5	31 " phosphorus.
				106.5 " chlorine.

Name.	*d.*	$d \times 28.88$	*M.*	Constituents.
Phosphorus oxichloride,	5.40	155.9	153.5	31 parts phosphorus. 16 " oxygen. 106.5 " chlorine.
Phosphorus sulphochloride,	5.88	169.8	169.5	31 " phosphorus. 32 " sulphur. 106.5 " chlorine.
Triethyl phosphine oxide,	4.60	132.8	134	31 " phosphorus. 16 " oxygen. 72 " carbon. 15 " hydrogen.
Phosphorus pentasulphide,	7.65	220.9	222	62 " phosphorus. 160 " sulphur.
Selenium dioxide,	4.03	116.4	110	78 " selenium. 32 " oxygen.
Silicic chloride,	5.94	171.5	170	28 " silicon. 142 " chlorine.
Silicic fluoride,	3.6	104	104	28 " silicon. 76 " fluorine.
Silicic iodide,	19.1	551.6	536	28 " silicon. 508 " iodine.
Silicon ethyl,	5.14	148.4	144	28 " silicon. 96 " carbon. 20 " hydrogen.
Silicic mercaptan,	5.78	166 9	167.5	28 " silicon. 106.5 " chlorine. 32 " sulphur. 1 part hydrogen.
Sulphur dioxide,	2.247	64.9	64	32 parts sulphur. 32 " oxygen.
Sulphur trioxide,	3.01	86.9	80	32 " sulphur. 48 " oxygen.
Sulphuryl chloride,	4.67	134.8	135	32 " sulphur. 32 " oxygen. 71 " chlorine.
Hydrogen sulphide,	1.191	34.4	34	32 " sulphur. 2 " hydrogen.
Tantalic chloride,	12.9	372.5	359.8	182.3 " tantalum. 177.5 " chlorine.
Thallic chloride,	8.15	235.4	238.7	203.2 " thallium. 35.5 " chlorine.
Stannous chloride,	12.96	374.3	378	236 " tin. 142 " chlorine.

Name.	*d.*	$d \times 28.88$	*M.*	Constituents.
Stannic chloride, .	9.20	265.7	260	118 parts tin.
				142 " chlorine.
Tin ethyl, . .	8.02	231.6	234	118 " tin.
				96 " carbon.
				20 " hydrogen.
Tin triethyl chloride,	8.43	243.4	240.5	118 " tin.
				35.5 " chlorine.
				72 " carbon.
				15 " hydrogen.
Tin triethyl bromide,	9.92	286.5	285	118 " tin.
				80 " bromine.
				72 " carbon.
				15 " hydrogen.
Titanic chloride, .	6.84	197.5	192	50 " titanium.
				142 " chlorine.
Tungsten pentachloride, . . .	12.7	366.7	361.5	184 " tungsten.
				177.5 " chlorine.
Tungsten hexachloride, . . .	13.2	381.2	397	184 " tungsten.
				213 " chlorine.
Tungsten oxichloride,	11.84	342	342	184 " tungsten.
				16 " oxygen.
				142 " chlorine.
Uranium chloride, .	13.3	384.1	382	240 " uranium.
				142 " chlorine.
Uranium bromide, .	19.46	562	560	240 " uranium.
				320 " bromine.
Vanadium tetrachloride, . . .	6.78	195.8	193.3	51.3 " vanadium.
				142 " chlorine.
Vanadium acichloride,	6.11	176	173.8	51.3 " vanadium.
				16 " oxygen.
				106.5 " chlorine.
Zinc chloride, . .	4.57	132	136	65 " zinc.
				71 " chlorine.
Zinc methyl, . .	3.29	95.1	95.2	65.2 " zinc.
				24 " carbon.
				6 " hydrogen.
Zinc ethyl, . .	4.62	133	123.2	65.2 " zinc.
				48 " carbon.
				10 " hydrogen.
Zinc amyl, . .	6.95	200.7	207.2	65.2 " zinc.
				120 " carbon.
				22 " hydrogen.
Zirconium chloride, .	8.15	235.4	231.6	89.6 " zirconium.
				142 " chlorine.

This list contains compounds of thirty different elements and, by means of these compounds, supposing that they contain at least one of their elements in the smallest possible quantity, we can determine the atomic weights of the elements concerned. It will be seen, however, that, whereas the hypothesis of Avogadro furnishes us with a principle which enables us to state positively what the molecular weight of any gaseous compound is, it does not furnish a means for the determination of atomic weights directly. After examining the various compounds of an element, we select that one which contains the smallest quantity of the element in the molecule, and then, without further proof, we say this smallest quantity represents the atom. Thus it is evident that the atomic weights, as determined by this method, rest upon a more or less doubtful basis. For practical purposes, however, this is not a serious matter; inasmuch as, although we cannot assert that the weight found really represents the atomic weight, we can assert that it represents the weight of that portion of the element which conducts itself as an atom, *i. e.*, throughout the whole series of changes which it undergoes in its compounds it is indivisible.

Other Proofs of the Fact that the Molecules of Elements contain more than one Atom.—It has been stated above that the molecules of elements contain, in almost all cases, more than one atom; and it has been shown that, if the hypothesis of Avogadro be accepted, we are necessarily led to this conclusion by a simple consideration of the molecular weights of elements and their compounds. The question naturally arises: Is there any evidence independent of Avogadro's hypothesis, that the molecules of elements consist of more than one atom? There are at least some indications that this is the fact.

A number of the elements, as we ordinarily meet with them in the free state, conduct themselves as comparatively neutral bodies. Take, for instance, hydrogen. As a gas, this element possesses very little affinity for most other elements and compounds. We may bring it in direct contact with most substances without effecting any change whatever in these substances. If, however, we set it free from one of its compounds, and, at the moment it is set free, allow it to act upon some other body, we find that it is a compara-

tively active element, capable of effecting very material changes in other substances. The same is true of oxygen, nitrogen, and other elements. They are much more active in the *status nascendi* than in the free state. How shall we explain this? This can be done most readily by supposing the molecules of these elements, in the free state, to contain more than one atom bound together by chemism. Now, if it be required that an element thus constituted shall combine with another body, it is first necessary that the force which holds together the atoms be overcome; the atoms must be torn asunder before they can act as atoms; or, in other words, a decomposition must be effected before the required combination can take place.

Sometimes the attraction exerted by an atom of one element for an atom of another is so strong that this decomposition is effected, and the combination then takes place. Thus, if we bring hydrogen and chlorine together, both in the free state, they combine. In this case, the chlorine atom attracts the hydrogen atom more strongly than the hydrogen atom attracts its fellow, or the chlorine atom its own chlorine atom. On the other hand, numerous instances of the opposite kind might be adduced. One will suffice for the purpose of illustration. When hydrogen gas is passed through nitric acid no change takes place. But, if we dissolve zinc in nitric acid, a portion of the acid is decomposed by the hydrogen evolved. The hydrogen atoms, set free from the nitric acid, find the acid present, and act upon it in preference to combining to form free hydrogen; the elements in combination with nitrogen are forcibly removed and the hydrogen takes their place, forming ammonia.

Ordinary oxygen contains two atoms in the molecule. Ozone, another variety of oxygen, has the density 1.658, from which we find its molecular weight = 48. Now as the atomic weight of oxygen, according to previous determinations, is 16, it follows that the molecule of ozone contains three atoms. The difference between the two forms of oxygen is thus readily seen. Ozone is comparatively unstable. It gives up its extra atom with great ease to bodies with which it comes in contact, and causes thus an energetic oxidation. When heated up to 300°, it is also decomposed, forming ordinary oxygen, and then an increase of volume is observed. In this case, if no foreign body be present with which the liberated atom can unite, it unites

with another atom of the same kind. When it acts upon other bodies, the original volume of the gas remains unchanged. It thus appears that the two atoms of the molecule of ordinary oxygen are held together more firmly than the three atoms in the molecule of ozone. Here, then, again the different actions of the two varieties can apparently be best explained by supposing in each case the molecule to consist of more than one atom.

These and other similar considerations serve to strengthen the conclusion which was logically deduced from Avogadro's hypothesis, and hence, in turn, to increase the probability that the hypothesis is the expression of a natural law.

It must be acknowledged that the above arguments based upon a consideration of the nascent state are far from convincing. We have fallen into the way of explaining the active condition of elements in the nascent state by asserting, as though it were an established fact, that the molecule of most elements in the free state consists of two atoms, and that in this state it must hence be less active than it is when the atoms are uncombined. While this is plausible, it must not be forgotten that, up to the present, it is almost pure hypothesis, and that the facts are capable of quite a different intrepretation.

Molecular Formulas of Gaseous Compounds.—When the atomic weights of the elements are once determined, the rule of Avogadro, taken together with chemical analysis, is sufficient to enable us to determine the molecular formulas of gaseous chemical compounds; a problem, the solution of which without this rule is in many cases exceedingly difficult, and, indeed, at times impossible. Let us suppose the atomic weights of carbon (12), hydrogen (1), and oxygen (16) to be known. We analyze a certain compound, and find that it contains 37.50 per cent. carbon, 12.50 per cent. hydrogen, and 50.00 per cent. oxygen. This gives the atomic proportion 1 of carbon, 4 of hydrogen, and 1 of oxygen; and hence the simplest formula we can assign to the compound is CH_4O. But there is nothing thus far to prevent our acceptance of one of the formulas $C_2H_8O_2$ or $C_3H_{12}O_4$, etc., all of which satisfy the results of the analysis. We now determine the molecular weight by Avogadro's rule, and find it to be 32; and, as the sum

of the weights of the atoms in a molecule of a compound of the formula CH_4O is 32, we recognize this latter as the correct formula.

Apparent Exceptions.—All formulas of chemical compounds at present employed are intended to represent molecules of the compounds. They are molecular formulas. They represent those amounts of the bodies which, in a gaseous condition, would occupy the same space as a molecule of hydrogen. If we take two volumes of hydrogen as the standard of comparison, then the formulas of compounds represent two volumes of the same size. To this there are apparent exceptions. When ammonia acts upon hydrochloric acid, the two gases combine in the proportion of 1 vol. of the one to 1 vol. of the other, forming a solid compound which contains 26.17 per cent. nitrogen, 7.48 per cent. hydrogen, and 66.35 per cent. chlorine. This gives the atomic proportion 1 nitrogen, 4 hydrogen, and 1 chlorine; and the simplest formula we can assign to the compound, provided the atomic weights of nitrogen, hydrogen, and chlorine are respectively 14, 1, and 35.5, is NH_4Cl. On now determining the molecular weight by Avogadro's rule, this is found to be 26.75, or half of that required by the above formula. Evidently, it is impossible for a molecule made up of chlorine, nitrogen, and hydrogen, with the atomic weights above assigned to them, to have as small a weight as 26.75; and, to satisfy the results of this determination, we would be obliged to write the formula $N_{\frac{1}{2}}H_2Cl_{\frac{1}{2}}$, and thus accept the existence of half atoms, which, according to the definition of atoms, is impossible. We might also imagine the atomic weight of nitrogen and chlorine, as already determined, to be just twice too great; for, if we assign to nitrogen the atomic weight 7, and to chlorine 17.7, we could write the formula of the compound NH_2Cl, and this compound would have the molecular weight 26.7, as determined by Avogadro's method. On the other hand, if 7 is the atomic weight of nitrogen, and 17.7 that of chlorine, then in all other compounds of nitrogen or chlorine, in which one atom has been supposed to exist in the molecule, we must necessarily accept the existence of two atoms in the molecule. But then all these compounds would not come under Avogadro's rule. Hence we see that the compound NH_4Cl appears to be an excep-

tion, and. if no satisfactory explanation can be found to account for this case, its existence is fatal to the rule. A satisfactory explanation can be offered, however, as follows:

If it can be proved that the vapor obtained from the compound NH_4Cl is not the vapor of this compound, but a mixture of the vapors of its constituent NH_3 and HCl, the case becomes a very simple one. Without entering into details, it may be mentioned that the results of the experiments made upon this subject have justified the assumption that, when the compound NH_4Cl is heated up to a temperature sufficiently high to cause its conversion into vapor, it becomes resolved into its constituents NH_3 and HCl, and that, when this mixture of two vapors is cooled down, the two again unite to form the original compound.

As NH_3 and HCl combine volume to volume, so the mixture of the two gases, obtained by heating NH_4Cl, consists of equal volumes of the two; and the specific gravity of this mixed vapor should be the mean of the specific gravities of its constituents. The specific gravity of NH_3 is 0.597, that of HCl is 1.247; the specific gravity of a mixture of the two would be $\frac{0.597+1.247}{2}=0.922$; and this specific gravity, if supposed to be that of a chemical compound, would lead to the molecular weight 26.6. The number 0.922 is, indeed, that found as the specific gravity of the vapor of NH_4Cl, and it will thus be seen that the fact can be satisfactorily explained without giving up our belief in the correctness of Avogadro's hypothesis.

The compound phosphorus pentachloride, PCl_5, was also at one time supposed to form an exception to the rule. The specific gravity of its vapor was found to be 3.66, from which was calculated the molecular weight 105.7, half that required by the formula PCl_5. It has been shown, however, that above a certain temperature the molecule of PCl_5 breaks up into a molecule of PCl_3 and a molecule of Cl_2. The vapor from PCl_5 is a mixture of two vapors, and the mean specific gravity of the two is the specific gravity found. The specific gravity of the vapor of PCl_3 is 4.88; that of Cl is 2.45; mean specific gravity $\frac{4.88+2.45}{2}=3.666$. In this case it has further been shown that the breaking up of the molecule takes place gradually; for the specific gravity of

the vapor decreases from 5.08 to 3.66, as the temperature is elevated from 182° to 300°, at which latter temperature the decomposition appears to be complete, no further decrease in specific gravity being noticed when the vapor is heated still higher.

It has further been shown that when the specific gravity of the vapor of phosphorus pentachloride, PCl_5, is determined in the presence of the trichloride, PCl_3, its decomposition is prevented, and the specific gravity found is that which theory requires for a compound of the formula PCl_5. The mean result of 7 determinations was 7.226, whereas, the theory requires 7.217. From this it is evident that the hypothesis of Avogadro is as valid for the compound PCl_5 as for other compounds.

A third example of this kind of decomposition by increase of temperature is met with in the case of the compound NO_2. This body, at a low temperature, consists of colorless crystals. At a slightly elevated temperature these crystals change to a yellow liquid. The liquid boils at 20–30°, and is then converted into a gas of a reddish-brown color, and as the temperature of the gas increases, the intensity of the color also increases. The specific gravity of the gas decreases with this elevation of temperature; hence, it is supposed that the body, at a low temperature, must be represented by the formula N_2O_4, but that the molecule is broken up by an elevation of temperature, forming two molecules of NO_2. The latter is strongly colored, and the more of it there is present in the mixture, the more intense is the color of the gas.

Among chemical compounds there are very few, indeed, that conduct themselves in the manner of the three just described. As regards some of these, good proof can be given of the fact that their molecules are broken up by the conversion into vapor, and hence, the apparently abnormal specific gravities observed for these vapors find a simple explanation. As regards others, although positive proof to the same effect may indeed be lacking as yet, still strong indications are presented that the abnormal densities may be referred to the same cause. So that, up to the present, not only is no fact known that speaks strongly against Avogadro's hypothesis, but, on the contrary, new developments, increased knowledge are constantly tending to strengthen it. It forms, to-day, by far the most reliable means for the

determination of molecular weights of compounds and elements; and we have seen how, secondarily, it aids us in determining atomic weights. But, in order that it may be useful, it is necessary that the compound which we desire to study, shall be capable of conversion into vapor, or, if it be an element under consideration, that at least one of the compounds of this element be gaseous or volatile. Only a comparatively small number of compounds satisfy these conditions, and of the 66 elements, only 36 (see List, pp. 46–50) enter into the composition of these compounds. With no other means, then, at our command, the work would be incomplete. It is necessary that some other method shall be introduced which shall be applicable to those elements not covered by Avogadro's rule, *i. e.*, those elements which are themselves incapable of conversion into vapor, and which do not enter into the composition of gaseous or volatile compounds.

III.

EXAMINATION OF SOLID ELEMENTS AND COMPOUNDS.

Specific Heat.—It has been noticed that, when equal weights of different substances are exposed to heat from the same source, they have different temperatures at the end of the same period of time. From this we conclude that to raise equal weights of different substances through the same number of degrees of temperature, different quantities of heat are necessary. Given exactly the same heating power, it takes about 32 times as long to raise the temperature of a pound of water 10, 20, or 30 degrees as it takes to raise the temperature of a pound of mercury the same number of degrees; or it takes 32 *times as much heat* to raise the temperature of a pound of water 10, 20, or 30 degrees as it takes to raise the temperature of a pound of mercury the same number of degrees. The quantity of heat required to raise the temperature of a given weight of any substance a given number of degrees, as compared with the quantity of heat required to raise the temperature of the same weight of water the same number of degrees, is called the specific heat of the substance. The quantity of heat required to raise the temperature of a pound of water 1 degree Centigrade, may be conveniently adopted as the thermal unit. We then speak of the specific heat of water as = 1; and the specific heat of any other body is the relative quantity of heat necessary to raise the temperature of a pound of this body 1 degree Centigrade, taking the above thermal unit as the standard. The specific heat of mercury, according to the results of the experiment mentioned, is 0.03332; that of gold is found to be 0.03244, etc., etc. The meaning of these numbers will be readily seen.

Relations between Specific Heat and Atomic Weight.—Now, when the solid elements are examined with reference to their specific heats, a very simple relation is found to exist between the numbers expressing the specific heats and

the atomic weights. This relation will be made clear by a consideration of a few cases actually examined:

Element.	Specific heat.	Atomic weight.
Silver, ...	0.0570	108
Zinc, ...	0.0955	65.2
Cadmium, ...	0.0567	112
Copper, ...	0.0952	63.4
Tin, ...	0.0562	118

It will be seen by an examination of this table that the atomic weights are inversely proportional to the specific heats. We have

108 : 65.2 :: 0.0955 : 0.0570;
112 : 63.4 :: 0.0952 : 0.0567;
108 : 118 :: 0.0562 : 0.0570, etc.

These proportions are only approximately correct; but it must be remembered that the means for the determination of atomic weights are capable of much greater refinement than those employed for the determination of specific heats. There is much greater liability of error in the latter determinations than in the former. Hence, such slight variations from absolute agreement in these proportions can occasion no surprise. The agreement is sufficiently close to indicate a decided and undoubted connection between the two sets of numbers. This connection may be stated in another way: The product of the atomic weight into the specific heat is a constant quantity for the elements examined. Thus, in the above cases:

108 × 0 057 = 6.15
65.2 × 0.0955 = 6.22
112 × 0 0567 = 6.35
63.4 × 0.0952 = 6.03
118 × 0.0562 = 6.63

For the same weights, then, the quantities of heat necessary to elevate the temperature of the elements one degree vary. The quantity necessary to elevate the temperature of an atom one degree would, of course, be represented by the variable quantity multiplied by the atomic weight, and this product, in the cases cited, we find to be represented by a constant.

Investigations of Dulong and Petit.—In the year 1819 attention was first called to the above relation by Dulong

and Petit, and, having examined a large number of elements, they felt justified in propounding the law: *The atoms of all elementary bodies have exactly the same capacity for heat.* This is simply a generalization from the facts stated, and is another way of stating that, to raise the temperature of atoms one degree, the same quantity of heat is always necessary.

If the law propounded is in reality a law, it will be readily seen that a new means is given for the determination of the atomic weights of elements of which we can know the specific heat. If we assume that the constant number obtained by multiplying the specific heats by the atomic weights is 6.25, which is about the average of the different values found, then it is plain that, if we divide this number by the specific heat of an element, we shall obtain a number which approximately represents the atomic weight. If we call the atomic weight A, and the specific heat H, the following formula will express the relation:

$$A = \frac{6.25}{H}$$

In order that this might hold good for all the elements investigated by Dulong and Petit, they found it necessary to change the atomic weights of four of the metals; just as it had been necessary to change certain of the atomic weights in order that Avogadro's hypothesis might hold good in all cases. But, as these atomic weights had been determined purely empirically, and thus rested upon a questionable basis, there could be no serious objection to the change. Notwithstanding the simplicity of the law, its validity was not, however, immediately acknowledged.

Investigations of Neumann and Regnault.—Twelve years later (1831), Neumann published investigations on the specific heat of chemical compounds, and showed that, for bodies of similar composition, the specific heats are inversely proportional to the molecular weights of the compounds, or the molecules of different compounds have equal capacity for heat; *i. e.*, for bodies of similar composition, the product of the molecular weight (M) into the specific heat (H) is a constant quantity. For example, the specific heat of lead iodide is 0.0427; that of lead bromide is 0.0533; that of lead chloride is 0.0664; the molecular weights of these

compounds are respectively 461, 367, and 278. The products $M \times H$ are as follows:

For lead iodide, . . $461 \times 0.0427 = 19.68$
" bromide, . . $367 \times 0.0533 = 19.56$
" chloride, . . $278 \times 0.0664 = 18.46$

Further, the specific heat of barium chloride is 0.0902; that of strontium chloride is 0.1199; that of calcium chloride is 0.1642. The molecular weights of these compounds are respectively 208, 158.5, and 111. The products $M \times H$ are:

For barium chloride, . . $208 \times 0.0902 = 18.76$
" strontium chloride, . $158.5 \times 0.1199 = 19.00$
" calcium chloride, . . $111 \times 0.1642 = 18.22$

Subsequently, similar investigations were carried out in connection with a large number of compounds, and it is particularly to the labors of Regnault (1840) that the development of this branch of the subject is due. The result attained may be stated concisely thus: *The elements possess essentially the same specific heat, whether they exist in a free state or in combination.*

To show how this conclusion may be deduced from known facts, let us take again the case of lead iodide. Lead has the specific heat 0.0307, iodine 0.0541. Multiplying by the atomic weights, we have $0.0307 \times 207 = 6.35$; and $0.0541 \times 127 = 6.87$; but, as can be determined, there are two atoms of iodine in the molecule of lead iodide, hence the atomic heat 6.87 must be multiplied by 2, which gives 15.74. To raise the constituents of lead iodide one degree in temperature would then require an amount of heat represented by the number $6.35 + 13.74 = 20.09$, and we have found that the amount of heat necessary to raise lead iodide as a compound one degree in temperature is 19.68. As these results may be looked upon as coincident, it follows that the specific heat of the elements in this case is the same whether the elements be in combination or in the free state.

Determination of Atomic Weights by a Study of the Specific Heat of Compounds.—Adopting the principle made clear in the above remarks, we see that a study of the specific heat of compound bodies may aid us in the determination of atomic weights; for we may ascertain the specific heat of an element, even where this cannot be determined directly. It is difficult, for instance, to ascertain the specific heat of

gaseous elements directly, and yet, as these elements form solid compounds, the specific heat of the latter may be determined, and thus, indirectly, that of the gaseous elements.

To illustrate by an example, let us consider the case of chlorine. Suppose it be required to determine the atomic weight of this element by means of specific heat determinations. We cannot determine the specific heat of the element directly. It forms compounds, however, with other elements, the specific heats and atomic weights of which may be determined. It combines with lead. The specific heat of lead is found to be 0.0307, which, according to the law of Dulong and Petit, gives the atomic weight 207. Now, in lead chloride, we find that 207 parts by weight of lead are combined with 71 parts by weight of chlorine; or, with 1 atom of lead, there is combined an amount of chlorine weighing 71 times as much as 1 atom of hydrogen. But we do not know how many atoms of chlorine this weight represents. It cannot be less than one, but it may be 2, 3, 4, or more atoms, as far as we know. We determine the specific heat of lead chloride, and find it to be 0.0664. We have assumed that the molecular heat of a compound (*i. e.*, the product of the molecular weight into the specific heat) is equal to the sum of the atomic heats (*i. e.*, the product of the atomic weight into the specific heat) of the atoms contained in the compound; or

$$M \times H = A \times H + A' \times H' + A'' \times H'' \ldots .$$

But, as the products $A \times H$, $A' \times H'$, $A'' \times H''$ have been shown to be constant and equal to about 6.25, we may simplify this equation as follows:

$$M \times H = n6.25;$$

and from this equation, M and H being known, we can determine the value of n, or the number of atoms contained in the molecule.

In the case under consideration we have:

$$278 \times 0.0664 = n6.25;$$
$$18.46 = n6.25;$$
$$n = 3.$$

We then conclude that in the molecule (278 parts) of lead chloride there are contained three atoms. But we know that there is one atom of lead; hence, there must be

two atoms of chlorine; and, as two atoms weigh 71, the atomic weight of chlorine is 35.5, the same as that found by means of Avogadro's method.

Further, we have other compounds in each of which 71 parts of chlorine are combined with a certain quantity of another element, and the molecular heat of which is the same as that of lead chloride. From the latter fact we conclude that there are also three atoms contained in the molecules of these compounds, and hence, that quantity of an element which, in these compounds, is combined with 71 parts of chlorine, represents the atomic weight. Thus, we have for the molecular heat of barium, strontium, and calcium chlorides 18.76, 19.00 and 18.22, respectively, numbers which may be considered the same as 18.46, the molecular heat of lead chloride; and in these compounds there are 137 parts barium, 87.5 parts strontium, and 40 parts calcium, combined with 71 parts chlorine. We hence conclude that 137, 87.5 and 40 are respectively the atomic weights of barium, strontium, and calcium, although direct determinations of the specific heat have been made in only two of these cases.

Of course, just as we have thus indirectly determined the atomic weights of certain elements, we can also determine the unknown specific heats of these same elements by a slight variation of the process. Take lead chloride. The molecular heat of this compound is 18.46; the atomic heat of lead is 6.35; hence, we have $18.46 - 6.35 = 12.11$, for twice the atomic heat of chlorine, there being two atoms of chlorine contained in the compound. This gives the atomic heat $\frac{12.11}{2} = 6.06$ for chlorine; and dividing by the atomic weight, we obtain $\frac{6.06}{35.5} = 0.1707$, which, accordingly, would represent the specific heat of chlorine, if the gases were subject to precisely the same law as solids.

By processes like those described, the atomic weights of a number of the elements have been determined, and, in many cases, the results obtained have been considered decisive.

The following tables (I.) of elements, and (II.) of compounds, contain the numbers actually obtained and the results deduced from them. The numbers under *H* are those representing the specific heats of the elements; those under *A* are the atomic weights as determined by analytical

methods, aided by the rule of Avogadro, or that of Dulong and Petit; finally, in the last column, is the product of the atomic weight into the corresponding specific heat ($A \times H$), called, for convenience sake, the atomic heat.

	H.	A.	$A \times H$.
Lithium,	0.941	7	6.6
Sodium,	0.293	23	6.7
Magnesium,	0.250	24	6.0
Aluminium,	0.214	27.4	5.9
Silicon,	0.173	28	4.8
Phosphorus,	0.174	31	5.4
Sulphur,	0.178	32	5.7
Potassium,	0.166	39	6.5
Calcium,	0.170	40	6.8
Chromium,	0.100	52	5.2
Manganese,	0.122	55	6.7
Iron,	0.114	56	6.4
Cobalt,	0.107	59	6.2
Nickel,	0.109	59	6.4
Copper,	0.0952	63.4	6.0
Zinc,	0.0955	65.2	6.2
Arsenic,	0.0814	75	6.1
Selenium,	0.0746	79.4	5.9
Bromine (solid),	0.0843	80	6.7
Molybdenum,	0.0722	92	6.6
Ruthenium,	0.0611	104.4	6.4
Rhodium,	0.0580	104.4	6.1
Palladium,	0.0593	106.6	6.3
Silver,	0.0570	108	6.2
Cadmium,	0.0567	112	6.4
Indium,	0.0570	113.4	6.5
Tin,	0.0562	118	6.6
Antimony,	0.0508	122	6.2
Iodine,	0.0541	127	6.9
Tellurium,	0.0474	128	6.1
Tungsten,	0.0334	184	6.1
Gold,	0.0324	197	6.4
Platinum,	0.0324	197.4	6.4
Iridium,	0.0326	198	6.5
Osmium,	0.0311	199.2	6.2
Mercury,	0.0317	200	6.3
Thallium,	0.0335	204	6.8
Lead,	0.0307	207	6.4
Bismuth,	0.0308	210	6.5

The following are some of the compounds which have been employed for the purpose of determining the atomic

weights of elements. The numbers under H are those representing the specific heats of the compounds; those under M are the molecular weights; the products $M \times H$ are the so-called molecular heats; n represents the number of atoms in the molecule of the compound.

	H.	M.	$M \times H$.	n.	$\frac{M \times H}{n}$.
$CoAs_2$, . .	0.0920	209	19.2	3	6.4
Ag_2S, . .	0.0746	248	18.5	3	6.2
Cu_2S, . .	0.1212	158.8	19.2	3	6.4
HgS, . .	0.052	232	12.1	2	6.1
NiS, . .	0.1281	91	11.6	2	5.8
PbS, . .	0.053	239	12.7	2	6.4
SnS, . .	0.0837	150	12.6	2	6.3
SnS_2, . .	0.1193	182	21.7	3	7.2
AgCl, . .	0.0911	143.5	13.1	2	6.6
CuCl, . .	0.1383	98.9	13.7	2	6.9
KCl, . .	0.1730	74.6	12.9	2	6.5
LiCl, . .	0.2821	42.5	12.0	2	6
NaCl, . .	0.2140	58.5	12.5	2	6 3
$BaCl_2$, . .	0.0896	208	18.6	3	6.2
$CaCl_2$, . .	0.1642	111	18.2	3	6.1
$SrCl_2$, . .	0.1199	158.5	19.0	3	6.3
$HgCl_2$, . .	0.0689	271	18.7	3	6.2
$MgCl_2$, . .	0.1946	95	18.5	3	6.2
$MnCl_2$, . .	0.1425	126	18.0	3	6.0
$PbCl_2$, . .	0.0664	278	18.5	3	6.2

Exceptions to the Law of Dulong and Petit.—On examining these tables, we are struck by the fact that the product, $A \times H$, in the first, and the quotient, $\frac{M \times H}{n}$, in the second—although assumed to be constant in value—show a very considerable variation from the mean value, 6.25. For a large number of these cases, we are justified in concluding that the variations are due to the errors of observation in consequence of the imperfections of the methods employed for the determination of specific heat. Indeed, in all the cases cited in the above tables, the variations are hardly great enough to lead us to suspect the incorrectness of the law of Dulong and Petit. If, however, we consider the elements carbon, boron, and silicon, we shall find that under some circumstances entirely different results are reached, and we must admit that, for these elements at least, the law does not ap-

pear to hold good. This will be best seen by means of the following table, in which H is the specific heat; t, the temperature at which the determination was made; A, the atomic weight; and $A \times H$, the atomic heat. As these three elements form the most marked exceptions to the law, all the more reliable determinations of their specific heats are given, for reasons which will be clear.

	H.	t.	A.	$A \times H$.
Carbon:				
a. Diamond,	0.064	at — 50.5°	12	0.77
"	0.096	at — 10.6°	12	1.15
"	0.113	at + 10.7°	12	1.36
"	0.132	at 33.4°	12	1.58
"	0.153	at 58.4°	12	1.84
"	0.177	at 85.5°	12	2.12
"	0.222	at 140°	12	2.66
"	0.273	at 206.1°	12	3.28
"	0.303	at 247°	12	3.64
"	0.441	at 606.7°	12	5.29
"	0.449	at 806.5°	12	5.39
"	0.459	at 985°	12	5.51
b. Graphite,	0.114	at — 50.3°	12	1.37
"	0.199	at 61.3°	12	2.39
"	0.297	at 201.6°	12	3.56
"	0.445	at 641.9°	12	5.34
"	0.467	at 977.9°	12	5.60
c. Charcoal,	0.194	0° to 99.2°	12	2.33
"	0.239	0° to 223.6°	12	2.87
Silicon:				
Crystallized,	0.136	at — 39.8°	28	3.81
"	0.170	at + 21.6°	28	4.76
"	0.183	at 57.1°	28	5.12
"	0.190	at 86°	28	5.32
"	0.196	at 128.7°	28	5.49
"	0.201	at 184.3°	28	5.63
"	0.203	at 232.4°	28	5.68
Boron:				
Crystallized,*	0.192	at — 39.6°	11	2.11
"	0.238	at + 26.6°	11	2.62
"	0.274	at 76.7°	11	3.01
"	0.307	at 125.8°	11	3.38
"	0.338	at 177.2°	11	3.72
"	0.366	at 233.2°	11	4.03

* As has been shown by Hampe crystallized boron, whether the crystals be of the black or the yellow variety, is not the pure ele-

An examination of the above table will show that at ordinary temperatures the elements carbon, silicon, and boron do not follow the law of Dulong and Petit as it has been formulated. It will be seen, however, that as the temperature is raised the specific heat becomes greater until finally, in the cases of carbon and silicon, a point is reached beyond which there is no marked change. Thus at 600° the specific heat of the diamond is 0.441 and at 985° it is 0.449. That of silicon is 0.201 at 185° and 0.203 at 332°. At these temperatures the elements obey the law of Dulong and Petit. In the case of boron it will be observed that the highest temperature at which a determination of the specific heat has actually been made is 233.2°. Assuming that the rate of increase above 230° is the same as the rate between —40° and 230°, the specific heat would become 0.50 at about 600°, and this is the figure required by the law. The above facts may be conveniently stated in this form: The specific heats of the elements carbon, silicon, and boron increase gradually from the lowest temperature to certain points, when they remain practically constant for any further elevation of temperature. The point for carbon and boron is about 600°; that for silicon about 200°. At these temperatures, and above them, the elements have the following specific heats: carbon 0.46; boron 0.50; silicon 0.205. The products obtained by multiplying these figures by the atomic weights 12, 11, and 28, are 5.5, 5.5, and 5.8; so that carbon, boron, and silicon are not exceptions. The law of Dulong and Petit, however, is a little more complicated than as stated above, and should have the following form:

The specific heats of the elements vary with the temperature; but for every element there is a point, T, above which the variations are very slight. The product of the atomic weight into the constant value of the specific heat is nearly a constant, lying between 5.5 and 6.5.

To account for the variations in the specific heats of the elements, it has been suggested that we cannot in most cases determine the true specific heat. This is only that heat which goes to increase the temperature. In measuring specific heats, we usually deal with a complex quantity, viz., that heat which raises the temperature, together with

ment. The black crystals, according to this chemist, have the composition AlB_{12}, and the yellow crystals the composition $C_2Al_3B_{48}$.

that which performs internal work and that which performs external work. In the cases of solids and liquids, the external work performed is very small. The internal work is probably different in different cases, and may amount to considerable. The fact, that the specific heats of so many elements, when multiplied by the atomic weights of these elements, give the same product, indicates that in these cases the external work, like the specific heat, is inversely proportional to the atomic weights. It is evident, according to this, that, if the amount of internal work varies in different elements, the specific heat will also vary in such a way as to seem to conflict with the law. It remains then for the future to show how specific heat determinations can be made which shall be independent of the internal and external work. When this can be done, it is probable that the law of Dulong and Petit will be found to be a perfect law, without exceptions of any kind.

ISOMORPHISM AS FURNISHING A MEANS FOR DETERMINING ATOMIC WEIGHTS.—Another means, once considered valuable, for determining atomic weights is found in connection with isomorphism. It has long been known that some substances of entirely different composition have approximately the same crystalline form. This was explained by Mitscherlich (1819) by supposing that an equal number of atoms in different molecules causes the same crystalline form. A little later he proposed the following statement as probably representing the law of ismorphism:

> *An equal number of atoms, united in the same way, give the same crystalline form; and this crystalline form is independent of the chemical nature of the atoms, being only dependent on their number and arrangement.*

If this law were strictly true, it is plain that we should in many cases be able to determine atomic weights by its aid. A few examples will illustrate the method:

The two substances $BaCl_2+2H_2O$ and $BaBr_2+2H_2O$ are isomorphous. We may assume, then, that their molecules contain the same number of atoms, and, if we know the atomic weights of the constituents of the molecule $BaCl_2+2H_2O$, we can easily determine the atomic weight of the Br in the molecule $BaBr_2+2H_2O$. Further, the compounds CuAgS and CuCuS are isomorphous. Assuming that the molecules of each contain the same number of atoms, and

knowing the atomic weights of copper and sulphur, we obtain very readily the atomic weight of silver.

It cannot be denied that this method has been of service in the establishment of atomic weights. Nevertheless, it requires but a few examples to prove that, if to the term isomorphism we give the wide meaning implied in the wording of the law as stated above, the results reached by means of it are not reliable. The salts $BaMn_2O_8$, Na_2SO_4, and Na_2SeO_4 have the same crystalline form, and yet the best methods for determining formulas show that those given are the correct ones. If we were, in these cases, to assume that the number of atoms in each of the molecules is the same, we would reach results at variance with those obtained by our most reliable means. We see thus that, if the isomorphism of salts is employed as a means for the determination of atomic weights, the results must be looked upon as doubtful, unless the sense of the word isomorphism be changed.

Kopp holds that identity of crystalline form is not a sufficient basis for designating compounds as isomorphous, and that the term should be used in a much more restricted sense. If, according to this writer, a crystallized compound has the power of growing in a solution of another compound then the two may be regarded as isomorphous. Thus, as is well known, if a crystal of ordinary alum be placed in a solution of iron alum, it will grow in the same way that it would in the original solution. This power of forming overgrowths should be regarded as the true criterion of isomorphism. Understood in this sense the use of the expression isomorphism becomes much more restricted than it was when used in the old sense. There are many bodies which have the same crystalline form which are not isomorphous in the new sense.

In the foregoing, free use of the expression *Atomic Weights* has been made. Using the language of the atomic hypothesis, the methods for determining the *Atomic Weights* have been considered. It is well, however, before passing on to the next part of our subject to recall the fact that it cannot be asserted of the figures called atomic weights that they represent the relative weights of atoms. Whether they do or do not, they certainly have a close relation to certain important facts which lie at the foundation of all cases of chemical action. The laws of definite and multiple pro-

portions are the fundamental laws of chemistry. They are as firmly established as any laws of nature, and they are simply the expressions of facts observed. We can certainly select for each element some figure which itself will represent, or a multiple of which will represent, the proportion by weight in which this element enters into chemical action. The difficulty is to know which one to select. To get over the difficulty we study certain physical properties of the elements and their compounds, as the specific gravity of the vapor, the specific heat, the crystalline form, and determine the weights of the substances which, on this basis, seem to be analogous. We thus get figures which bear to each other certain relations very similar to those which the so-called atomic weights, determined by chemical methods, bear to each other. The similarity of the relations of the figures obtained by the different methods suggests a common cause, and we attempt to satisfy our desire to ascertain the cause by saying that the figures represent the relative weights of atoms. But the figures would be just as valuable without this hypothesis, and we might deal with all the facts of chemistry without referring to the possible existence of atoms.

IV.

PROPERTIES OF THE ELEMENTS AS FUNCTIONS OF THEIR ATOMIC WEIGHTS.

Natural Groups of Elements.—If we examine the list of elements and their atomic weights, we find that there are a number of well-marked groups, indicating some connection between the atomic weights and properties of the elements. Among these may be mentioned chlorine, bromine, and iodine; sulphur, selenium, and tellurium; lithium, sodium, and potassium. Arranging these according to their atomic weights, we have:

Cl	35.5	S	32	Li	7
Br	80	Se	79.5	Na	23
I	127	Te	128	K	39

If in each of these groups we add together the atomic weights of the first and last elements, and divide the sum by 2, we obtain very nearly the atomic weights of the middle members of the series: $\frac{35.5 + 127}{2} = 81.25$, $\frac{32 + 128}{2} = 80$, $\frac{7 + 39}{2} = 23$. We see, also, that the elements, whose atomic weights are thus closely connected, are themselves very closely allied in their properties. Considerations of this kind have led chemists, from time to time, to examine the atomic weights more closely, and, as a result of these examinations, it has been found that the connection above indicated is much more general than was at first supposed. A number of schemes have been devised for the purpose of showing this connection clearly, some of which are certainly worthy of attention. We shall consider here the schemes of D. Mendelejeff* and Lothar Meyer,† as they

* Zeitschrift für Chemie, 1869, 405, and Annalen der Chemie, 8 Suppl., 133.

† Annalen der Chemie, 7 Suppl., 356.

embody all that is good of other schemes and are themselves comparatively perfect.

The Scheme of Mendelejeff.—Mendelejeff first calls attention to the fact that, if all the light elements with atomic weights from 7 to 36 are arranged *in the order of their atomic weights*, the following remarkable table is obtained:

Li = 7;	Be = 9;	B = 11;	C = 12;	N = 14;	O = 16;	Fl = 19;
Na = 23;	Mg = 24;	Al = 27;	Si = 28;	P = 31;	S = 32;	Cl = 35.5.

In these two series, elements which we recognize as similar come to stand together as Li and Na, Mg and Be, C and Si, O and S, etc. The gradual change in the properties of the members of the series, as we pass from left to right, is noticed particularly, if we consider the compounds which the elements form. Thus, only the four last members combine with hydrogen, yielding compounds of the general formulas,

$$RH_4,\ RH_3,\ RH_2,\ RH.$$

The character of these hydrogen compounds also changes gradually, according to the position in the series. ClH is a marked acid of great stability, SH_2 is a weak acid decomposable by heat, PH_3 is not an acid, and is less stable than the preceding compounds, and this is still more true of SiH_4.

Considering the oxides of the members of the second series we have—

$$\underset{\text{or } MgO,}{Na_2O},\ \underset{}{Mg_2O_2},\ \underset{\text{or } SiO_2,}{Al_2O_3},\ \underset{}{Si_2O_4},\ \underset{\text{or } SO_3.}{P_2O_5},\ \underset{}{S_2O_6},\ \underset{}{Cl_2O_7}.$$

From left to right in this series the basic properties grow weaker and the acid properties stronger. Again, in the composition of the hydroxides, the same regularity is observed:

$$Na(OH),\ Mg(OH)_2,\ Al(OH)_3,\ Si(OH)_4,\ PO(OH)_3,\ SO_2(OH)_2,\ ClO_3(OH).$$

Another point to be noted is this: that, in the series with which we are dealing, the metals are at one end and the so-called non-metals at the other, while those elements which

are sometimes placed with the metals and sometimes with the non-metals, as for instance, Si, come in the middle.

But, just as the chemical properties undergo gradual change in the series mentioned, so also a corresponding change is noticed in the physical properties. To illustrate this, the specific gravities and the atomic volumes of the members of the second series are given:

	Na	Mg	Al	Si	P	S	Cl
Spec. gr.	0.97	1.75	2.67	2.49	1.84	2.06	1.33.
Atom. vol.	24	14	10	11	16	16	27

	Na_2O	Mg_2O_2	Al_2O_3	Si_2O_4	P_2O_5	S_2O_6	Cl_2O_7
Spec. gr.	2.8	3.7	4.0	2.6	2.7	1.9	?
Atom. vol.	22	22	25	45	55	82	?

Another series corresponding to the two already given is the following:

Ag = 108:	Cd = 112;	In = 113;	Sn = 118;	Sb = 120;	Te = 125?;	I = 127
Sp. gr. 10.5;	8.6;	7.4;	7.2;	6.7;	6.2;	4.9.

All the elements may be arranged in series similar to the above, and thus a very intimate connection between the atomic weights and the properties of the elements is shown to exist. It will be noticed that the changes in the properties of the elements are *periodic*. First, these properties change according to the increasing atomic weights, then they are repeated *in a new period* with the same regularity as in the preceding series. Such series as those already mentioned are called *small periods*. If H is placed in the first series, then Li, etc., come in the second series, Na, etc., in the third, etc.

But all the known elements cannot be arranged in the small periods, and what is much more important, the corresponding members of the even (4, 6, etc.) periods, or of the uneven (5, 7, etc.), resemble each other more closely than the members of the even periods resemble those of the uneven periods. This may be seen from the following example:

Fourth period:	K,	Ca,	Sc,	Ti,	V,	Cr,	Mn.
Fifth " :	Cu,	Zn,	Ga,	—	As,	Se,	Br.
Sixth " :	Rb,	Sr,	Y,	Zr,	Nb,	Mo,	—
Seventh " :	Ag,	Cd,	In,	Sn,	Sb,	Te,	I.

The members of the fourth and sixth periods resemble each other more closely than they resemble the members of the fifth or seventh periods; and the members of the fifth and seventh periods resemble each other closely. The last members of the even periods resemble in many respects the first members of the succeeding uneven series. Thus Cr and Mn in their basic oxides are similar to Cu and Zn. On the other hand, between the last members of the uneven periods and the first members of the succeeding even periods, there are very marked differences, as, for instance, between Br and Rb. Further, between the last members of the even periods and the first members of the uneven periods, all those elements which cannot be arranged in the small periods would, according to their atomic weights and properties, naturally come. Thus between Cr and Mn, on the one hand, and Cu and Zn, on the other, Fe, Co, and Ni would come; the following series being thus formed:

$$\text{Cr} = 52;\ \text{Mn} = 55;\ \text{Fe} = 56;\ \text{Co} = 58;\ \text{Ni} = 59;$$
$$\text{Cu} = 63;\ \text{Zn} = 65.$$

As Fe, Co, Ni follow the fourth period, so Ru, Rh, Pd follow the sixth period, Os, Ir, Pt follow the tenth period. Two small periods (an even and uneven), together with an intermediate series of the elements just mentioned, form a *large period*. As the intermediate members mentioned correspond to none of the seven small periods, they form an independent eighth group:

$$\text{Fe} = 56;\ \text{Co} = 58;\ \text{Ni} = 59,$$
$$\text{Ru} = 103;\ \text{Rh} = 104;\ \text{Pd} = 106,$$
$$\text{Os} = 192?;\ \text{Ir} = 193;\ \text{Pt} = 195.$$

The members of this group resemble each other in the same way as the corresponding members of the even periods, as, for instance, V, Nb, Ta, or Cr, Mo, W, and others.

The two following tables of Mendelejeff show clearly the relations described. In the first, the elements with their atomic weights are arranged in large periods; in the second, they are arranged in groups and series in such a manner as to distinctly indicate the differences in the even and uneven periods.

Series.	Group I. $\overline{R_2O}$	Group II. $\overline{RO}$	Group III. $\overline{R_2O_3}$	Group IV. RH_4 RO_2	Group V. RH_3 R_2O_5	Group VI. RH_2 RO_3	Group VII. RH R_2O_7	Group VIII. $\overline{RO_4}$
1	H = 1							
2	Li = 7	Be = 9	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27	Si = 28	P = 31	S = 32	Cl = 35.5	
4	K = 39	Ca = 40	Sc = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe=56, Co=58, Ni = 59, Cu = 63
5	(Cu = 63)	Zn = 65	Ga = 69	— = 72	As = 75	Se = 79	Br = 80	
6	Rb = 85	Sr = 87	Y = 89	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru=103, Rh=104, Pd=106, Ag=108
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 120	Te = 125?	I = 127	
8	Cs = 133	Ba = 137	La = 138	Ce = 142	Di = 146	—	—	— —
9	(—)	—	—	—	—	—	—	— —
10	—	—	Yb = 173	—	Ta = 182	W = 184	—	Os = 192?, Ir = 193, Pt = 195, Au=196
11	(Au = 196)	Hg = 200	Tl = 204	Pb = 206	Bi = 209	—	—	
12	—	—	—	Th = 231	—	U = 240	—	— — — —

			I.	II.	III.	IV.	V.	VI.
R_2O	I.		Li=7	K 39	Rb 85	Cs 133	— —	— —
RO	II.		Be=9	Ca 40	Sr 87	Ba 137	— —	— —
R_2O_3	III.		B=11	Sc 44	Y 89	La 138	Yb 173	— —
RO_2	IV.	(H_4C)	C=12	Ti 48	Zr 90	Ce 142	— —	Th 231
R_2O_5	V.	(H_3N)	N=14	V 51	Nb 94	Di 146	Ta 182	— —
RO_3	VI.	(H_2O)	O=16	Cr 52	Mo 96	— —	W 184	U 240
R_2O_7	VII.	(HF)	Fe=19	Mn 55	— —	— —	— —	— —
RO_4				Fe 56	Ru 103	— —	Os 192?	— —
	VIII.			Co 58	Rh 104	— —	Ir 193	— —
				Ni 59	Pd 106	— —	Pt 195	— —
R_2O	I.	H = 1	N=23	Cu 63	Ag 108	— —	Au 196	— —
RO	II.		Mg 24	Zn 65	Cd 112	— —	Hg 200	— —
R_2O_3	III.		Al 27	Ga 69	In 113	— —	Tl 204	— —
RO_2	IV.	(H_4R)	Si 28	?? 72	Sn 118	— —	Pb 206	— —
R_2O_5	V.	(H_3R)	P 31	As 75	Sb 120	— —	Bi 209	— —
RO_3	VI.	(H_2R)	S 32	Se 79	Te 125?	— —	— —	— —
R_2O_7	VII.	(HR)	Cl 35.5	Br 80	I 127	— —	— —	— —

It is not necessary to point out here all the properties of the elements which can be shown to vary in harmony with the changes of the atomic weights. What has already been said will suffice to indicate the principle involved in the construction of the tables of Mendelejeff. Close study of these tables does undoubtedly show that they contain some imperfections and apparent contradictions; still, these are not numerous enough or serious enough to materially interfere with the value of the tables. It is evident that the first condition for the construction of such tables is the correct determination of all the atomic weights. We have seen with what difficulty this determination is often attended, and how doubtful some of the results obtained are. When all the atomic weights shall have been accurately determined, and when all the properties, both physical and chemical, of the elements are known, then a table constructed on the principle of the above will, in all probability, show a perfect accordance between atomic weights and

properties. Perhaps then, too, the law of variation being known, it may be possible to propose a satisfactory theory in regard to the nature and conduct of atoms. Such a theory will be the legitimate result of the scientific chemical investigations now being carried on. The atomic hypothesis of Dalton, as at present accepted, will eventually prove to be but a part of a more comprehensive atomic theory, which latter will be the theory of chemistry, corresponding to the theory of heat and the theory of electricity in the broad domain of physics.

Mendelejeff originally proposed to use the *periodic law*, as he calls the simple rule governing the variations in the atomic weights and properties of the elements, for the purpose of determining the properties of undiscovered elements. When Table II. was first constructed, a member was wanting between calcium and titanium in the fourth series. The atomic weight of this element should be about 44, and its properties were also very nearly foretold from its position. Its oxide should have the composition R_2O_3, and its properties should bear the same relation to Al_2O_3 that those of CaO bear to MgO, or TiO_2 to SiO_2; consequently it should be a more energetic base than Al_2O_3 and should resemble it in corresponding compounds. Its sulphate should not be as easily soluble as aluminium sulphate, because calcium sulphate is more difficultly soluble than magnesium sulphate. Thus, throughout the whole list of properties, such comparisons were made, and the unknown element was more accurately described than some of those which have been known for a long time.

The prediction of this element, to which Mendelejeff gave the name ekabor, proved to be one of the most remarkable predictions in the field of chemistry. Within a few years the metal scandium was discovered, and was shown to be the predicted ekabor. In a similar way, gallium was predicted and described under the name of ekaluminium before its discovery.

Such speculations are, without doubt, very attractive, but we must not forget that the tables, which are used as their foundation, are more or less imperfect, and hence the conclusions drawn must necessarily be doubtful. On the other hand, the time will come when such speculations can be indulged in without risk of reaching doubtful results. The approach of this time will be hastened by just such

efforts as those of Mendelejeff to discover the law governing the connection between the atomic weights and the properties of the elements.

Lothar Meyer's Arrangement of the Elements.—Another arrangement of the elements showing the connection between the atomic weights and the properties of the elements is that of Lothar Meyer, already alluded to. His table* follows:

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Li							
7.01	?Be						
15.98	9.3	B					
Na	14.6	11.0	C				
22.99	Mg	16.3	11.97	N	O		
16.05	23.94	Al	16	14.01	15.96	F	
K	15.96	27.3	Si	16.95	16.02	19.1	
39.04	Ca	17.7	28	P	S	16.3	
24.3	39.90	?Sc	20	30.96	31.98	Cl	
Cu	25.0	45	Ti	20.2	20.4	35.37	
63.3	Zn	25	48	V	Cr	19.4	
21.9	64.9	Ga	23	51.2	52.4	Mn	
Rb	22.3	69.9	?	23.7	26.5	54.8	Fe | Co | Ni
85.2	Sr	19	72	As	Se	25.0	55.9 | 58.6 | 58.6
22.5	87.2	?Y | X | X	18	74.9	78.9	Br	
Ag	24.4	88 | 88.5 | 89	Zr	19	16.9	79.75	
107.66	Cd	25	90	Nb	Mo	19	
24.3	111.6	In	27.8	94	95.8	?	
Cs	25.2	113.4	Sn	28	30.5	99	Ru | Rh | Pd
132.0	Ba	26	117.8	Sb	Te	28	103.5 | 104.1 | 106.2
	136.8	La | Di | Ce		122	126.3	I	
?		139 | 140 | 141	?			126.53	
150	?Ng		142	?	?		
	150?	?		143	144	?	
?		158?	?			146	? | ? | ?
172	?		160	?	?		147 | 148 | 149
	173	Yb | X | X		162	164	?	
Au		174 | 176 | 177	?			165	
196.2	Hg		180	Ta	W		
	199.8	Tl		182	184	?	
?		203.6	Pb	28		187	Os | Ir | Pt
222	?		206.4	Bi	?		198? | 192.7 | 195
	227	X | X | X	27.5	210	212	?	
		229 | 231 | 232	?Th			213	
			233.9	?	?U		
				238	240		

* Die modernen Theorien der Chemie, Vierte Auflage. Breslau, 1880.

This table contains all the elements whose atomic weights have been determined with any degree of certainty. The series here represented resemble those in Mendelejeff's tables. Meyer further points out the connection between the atomic weights and the following properties of the elements: specific gravity in the solid condition, as shown by a comparison of the atomic volumes; metallic ductility, fusibility and volatility; crystalline form; influence upon the refraction of light; specific heat; conducting power for heat and electricity. The connection is not always very clearly discernible, but careful examination and the exclusion of sources of error as far as possible show that the connection is an actual one. It remains for the future to establish the close connection which exists, but which is thus far mostly hidden.

The position of the elements in the electro-chemical series is undoubtedly dependent on the position in the series of atomic weights, but it is such an exceedingly difficult thing to determine the proper order of the members in the electro-chemical series, that the connection between the two series is not plainly recognizable.

V.

VALENCE OR ATOMICITY OF ELEMENTS.

Definition.—The means for the determination of the molecular formulas of compounds have already been considered, and it has been shown that these formulas can be determined with a considerable degree of certainty by the aid of Avogadro's hypothesis. If we now examine the formulas as determined, certain new characteristics of the elements will present themselves. Let us take a few examples among the hydrogen compounds.

I.	II.	III.	IV.
ClH,	OH_2,	NH_3,	CH_4,
BrH,	SH_2,	AsH_3,	SiH_4.
IH,	SeH_2,	SbH_3,	
FlH,	TeH_2,	PH_3,	

We see here that Cl, Br, I, and Fl combine with H in the proportion of atom for atom; O, S, Se, and Te combine with H in the proportion of two atoms of hydrogen to one atom of the other element; in the compounds with N, As, Sb, and P, three atoms of hydrogen are in combination with one atom of the other element; and, lastly, four atoms of hydrogen are in combination with one atom of C or Si. The elements here mentioned are representatives of four great classes. If we consider the members of the first class, we shall find that the compounds which they form with each other are of the simplest kind. Indeed, they combine with each other only in one proportion, forming thus but one kind of compounds. If we take, for instance, hydrogen and chlorine and allow them to combine under the most varied conditions, the result is always hydrochloric acid, and this always contains 35.5 parts by weight of chlorine to 1 part by weight of hydrogen. The same is true of other members of the class, as bromine, potassium, sodium, etc. If, on the other hand, we consider the members of any of the other classes, we shall find that a greater variety presents itself in

their combinations, not only with each other, but with the elements of the first class. Oxygen combines with hydrogen in two proportions, forming water and hydrogen dioxide; nitrogen combines with oxygen in five proportions, forming nitrous oxide, nitric oxide, nitrogen dioxide, nitrous anhydride, and nitric anhydride; carbon combines with hydrogen in a very large number of proportions, forming several series of hydrocarbons. In the foregoing, we have an indication of some property of the elements which we have not thus far considered. In studying the elements now with reference to this new property, our first duty would plainly be to study all the compounds of the elements in order to get as broad a foundation of facts as possible. We would thus finally be enabled to draw the following conclusion:

Some elements combine with each other only in one proportion; others combine with each other and with other elements in more than one proportion.

This conclusion involves no hypothesis, but is the legitimate outgrowth of the known facts. The distinction made between the two classes of elements is fundamental.

But there must be some reason for the difference. Where shall we seek for it? If we accept the atomic hypothesis of Dalton, we must seek for the proximate causes of phenomena presented to us by masses of elements or their compounds in the atoms composing these masses. Here, then, we are to find in the atoms themselves the proximate cause of the new property of elements which we are considering. As, however, we can learn nothing of atoms directly, but only of masses of atoms, it is evident that this cause cannot be discovered, but must finally be imagined, just as the atom itself is still only imagined to exist. In other words, our ideas of atoms must become enlarged in such a way as to account for the new property, or a subordinate hypothesis must be formed to supplement the atomic hypothesis. Before forming this hypothesis, let us see whether we can learn anything more in regard to the new property than we have yet learned.

We have seen above that, on examining the formulas of chemical compounds, and comparing them with each other, the molecules of some of the compounds contain only 1 atom of hydrogen to each atom of the other element; in the molecules of other compounds we find 2 atoms of hydrogen to 1 atom of the other constituent; in others 3, and

in still others 4 atoms of hydrogen combined with 1 atom of some other element. In thus stating the number of atoms present in the molecules, we, of course, have left the domain of facts and have already entered that of hypothesis; still, the hypothesis involved in a molecular chemical formula, which has been determined by the aid of all means at our command, is one which we are justified in employing, and we accordingly add the knowledge, which we gain by means of this hypothesis, to that which we possess from the simple study of facts, and which is represented in our conclusions above drawn. Taking into consideration the sum total of our knowledge, as thus far stated, the simplest hypothesis which it is possible to form concerning the cause which we are striving to find, is the following: Every atom of an element has an inherent power of holding in combination a certain number of other atoms, this number being dependent upon the combining power of the atoms held in combination. The simplest atoms should represent the unit of this power, and we should distinguish between these simplest or unit-atoms and such as have the power of holding in combination 2, 3, 4, or more atoms.

Name of the New Property.—The property of the elements which we are studying has, in accordance with the simple hypothesis just given, been termed *atomicity*, *quantivalence*, or only *valence*.* The elements, which consist of the unit-atoms, are hence called *monatomic* or *univalent;* those, consisting of atoms which have twice the combining power of the unit-atoms, are called *diatomic* or *bivalent;* and, in a similar manner, we have *triatomic* or *trivalent*, *tetratomic* or

* In regard to the choice between the three expressions given, it may be said that the word valence seems to be less objectionable than the others which have been used, because it is the simplest, and, at the same time, it expresses all that we desire to express with reference to the property which it designates. Again, the word atomicity has been used in another sense, and hence its use might lead to confusion, some authors employing it in its first sense, others in the new and entirely different sense. By a monatomic, diatomic, etc., element is sometimes meant an element whose molecule consists of 1, 2, etc., atoms. As it is necessary to have words to express this latter sense, it seems desirable to leave the word atomicity and its adjective derivatives, monatomic, diatomic, etc., to serve this purpose, while we adopt the expression valence with the derivatives univalent, bivalent, trivalent, etc., for the purpose of designating the property under discussion.

quadrivalent, etc., elements. Further, the elements are called respectively *monads*, *dyads*, *triads*, *tetrads*, *pentads*, *hexads*, etc. Accordingly, of the elements in the brief table, given at the beginning of this article (p. 80), all those in the first lines are univalent; oxygen, sulphur, selenium, and tellurium are bivalent; nitrogen, arsenic, antimony, and phosphorus are trivalent; and carbon and silicon are quadrivalent.

Distinction between Valence and Affinity.—The property of valence must not be confounded with that of affinity. By affinity is usually meant the force with which one atom attracts another or others. Valence has apparently no connection with this force. An element may, in general terms, have a strong affinity for other elements, and yet be univalent. Another may possess but a weak affinity, and be quadrivalent. Thus, chlorine has a strong affinity for hydrogen, the two combine with great energy, yet they are both univalent elements. While carbon does not combine with chlorine with nearly as great energy as hydrogen does, it, nevertheless, is quadrivalent; its atom is capable of holding in combination 4 atoms of hydrogen. The two properties, valence and affinity, are possessed by every atom, and exhibit themselves every time that atoms act upon each other, the latter determining the energy of the action, the former the complexity of the resulting molecule.

Methods for Determining the Valence of the Elements.—The foundations upon which the conception of valence rests, and the conception itself being thus explained, let us inquire how we can determine the valence of the individual elements. We have recognized certain characteristics of the so-called univalent elements, and have seen that hydrogen belongs to this class. If, then, we are certain that hydrogen is univalent, we may employ it as a means of measuring the valence of other elements. The first general rules to guide us in the measurements are the following:

1. Those elements which combine with hydrogen in the proportion of 1 atom to 1 atom are univalent. Such, for instance, are chlorine, bromine, etc.

2. Those elements which combine with hydrogen in the proportion of 1 atom to 2 atoms of hydrogen are bivalent. Such, for instance, are oxygen, sulphur, etc.

3. Those elements which combine with hydrogen in the proportion of 1 atom to 3 atoms of hydrogen are trivalent. Such, for instance, are nitrogen, phosphorus, etc.

4. Those elements which combine with hydrogen in the proportion of 1 atom to 4 atoms of hydrogen are quadrivalent. Such, for instance, are carbon, silicon, etc.

But only comparatively a small number of the elements combine with hydrogen alone, so that this method must necessarily be of limited application. It is plain, however, that, if our conception of valence as above explained is correct, it is not necessary that we should employ hydrogen as our standard in measuring it. Any other univalent element may answer the same purpose. Having then first determined by means of hydrogen that chlorine and bromine are univalent, we may employ either of these as standards in the same manner as we employed hydrogen above. This would enable us to extend our measurements much further, and, eventually, to take in all the elements. In all cases in which the molecular formulas of the chlorine or hydrogen compounds of the elements can be determined by Avogadro's rule, the determination of the valence is, according to the rules given, a simple matter.

To illustrate the application of the method, let us take an example. Suppose we wish to determine the valence of oxygen. Oxygen forms two compounds with hydrogen. We analyze both of these compounds, and find that water contains the smallest proportion of oxygen to hydrogen. We assume, therefore, that in the molecule of water there is but 1 atom of oxygen, and we consequently take this compound for the purpose of making our determination. The molecular weight is found to be 18, and this, taken in conjunction with the results of the analyses, shows us that 16 parts of oxygen are combined with 2 parts of hydrogen. The atomic weight of hydrogen is already known to be 1. Hence 1 atom of oxygen is combined with 2 atoms of hydrogen, and hence, further, oxygen is a bivalent element.

Insufficiency of the Hypothesis.—In attempting to subdivide the elements into classes according to their valence, difficulties are met with, and these are so great that the hypothesis as already given proves inadequate, and must undergo change in order to be in harmony with the facts. The conception of valence, with which we have been deal-

ing, is the simplest which is held. It is, too, the first form in which it was brought to light. For these reasons it has been explained in full. It is now necessary, however, to show in what respects it is inadequate, and to show what changes it has undergone.

The original form of the hypothesis, as above stated, is: Every atom has an inherent power of holding in combination a certain number of other atoms, this number being dependent upon the combining power of the atoms held in combination.

According to this, phosphorus, which combines with hydrogen, forming the compound PH_3, ought, in combining with chlorine, to form the compound PCl_3, and there stop. Nitrogen, which forms the compound NH_3, ought to show itself as a trivalent element wherever it is met with. In the case of phosphorus, however, we have not only the chlorine compound PCl_3, but another, PCl_5; in the case of nitrogen, too, we have not only a whole series of compounds in which it plays the part of a trivalent element, but also a very large series in which it just as surely plays the part of a quinquivalent element. Thus we have, on the one hand, ammonia, NH_3, hydroxylamine, $\overset{III}{N}\overset{II}{H_2}(\overset{I}{OH})$, nitrous acid, $\overset{III}{N}\overset{II}{O}(\overset{I}{OH})$, etc., in which nitrogen is trivalent; while, on the other hand, we have ammonium chloride, $\overset{V}{N}\overset{IV}{H_4}\overset{I}{Cl}$, and the whole list of ammonium salts in which nitrogen is quinquivalent. A number of other instances could be given, showing that one and the same element exhibits different combining powers in different compounds, so that, if we attempted to classify the elements according to the valence, we would place the same element now with the trivalent and now with the quinquivalent; another would find its place with the bivalent and again with the quadrivalent, according as one or another compound of these elements is taken as the means of judging of the valence. Plainly, then, the conception of valence needs enlargement, for, as above stated, it has not a true foundation of facts.

Atomic and Molecular Compounds.—The difficulty just indicated was early recognized, and an attempt was made to surmount it by introducing another hypothesis in regard to the nature of chemical compounds. According to this

new hypothesis, there are two kinds of chemical compounds, which are called *atomic* and *molecular*. In the former we have the true chemical compounds, in the sense in which we have understood that expression from the beginning. In these, the atoms exhibit all the properties which we have thus far recognized as belonging to them—including valence. By virtue of these properties, the compounds have their existence. In the molecular compounds, on the other hand, a new force is supposed to act, this force being distinct from the interatomic force, and acting in a peculiar way between molecules. The molecules are supposed to be first formed by means of chemism, etc., and, when these have been formed, all that can be effected by valence has been effected. But now it is further supposed that the molecules thus formed have an attractive power and combining power of their own, by virtue of which the molecular compounds are formed. The most common examples of molecular compounds are salts containing water of crystallization. These are formed by virtue of the attraction of the molecules of the salt for the molecules of the water. But, according to the propounder of this hypothesis, we have further examples of molecular compounds in phosphorus chloride, PCl_5, and in ammonium chloride, NH_4Cl, In the former, a molecule of PCl_3, a true atomic compound, holds in combination a molecule of chlorine (Cl_2), also an atomic compound. In the latter, a molecule of NH_3. an atomic compound, holds in combination a molecule of hydrochloric acid, also an atomic compound.

Foundation for the Distinction between Atomic and Molecular Compounds.—Of course, in order that such an hypothesis as that under consideration should be at all permissible, it must be shown that there are differences between those compounds which are called molecular, and those which are called atomic. To a certain extent this is possible. In the case of salts containing water of crystallization, there can, at least usually, be no difficulty in recognizing that the force holding together the salt and the water is of a different nature from that which holds the constituents of the salt together, or that which holds the constituents of the water together. It is only necessary to heat the compounds gently in order to overcome the attraction and cause the breaking up of the complex molecule; in some cases, indeed, the attraction is so weak that it is only neces-

sary to expose the compound to the air, when the water passes off in the form of vapor, leaving the molecules of the salt intact. This weakness of the union is then a principal characteristic of molecular combination.

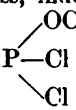
Now, if we examine the compounds above referred to, viz., PCl_5 and NH_4Cl, we find that they possess this characteristic. It has been shown, when considering the cases of anomalous specific gravities of vapors, that, when PCl_5 and NH_4Cl are heated to a sufficient degree to convert them into vapor, they are broken up into PCl_3 and Cl_2, and NH_3 and HCl, just as the crystallized salts lose their water of crystallization by being heated. So, also, in a number of other cases, it can be shown to be true that compounds, which we must consider as molecular in order to explain their existence and yet retain the hypothesis of valence, as above stated, break up under the influence of heat into simpler molecules.

We thus see that there is some foundation for assuming the existence of molecular compounds as distinct from atomic compounds. But how does this help us in surmounting the difficulty already met with in attempting to apply the principle of the hypothesis of valence for the purpose of classifying the elements?

Use of the Distinction.—It is plain that atomic compounds are the only ones which we can employ for the purpose of determining the valence of atoms. Thus, the only chlorine compound of phosphorus which we could employ for the purpose of determining the valence of phosphorus is PCl_3. The other compound PCl_5, the existence of which would seem to indicate that phosphorus is quinquivalent as well as trivalent, being a molecular compound, is formed independently of the valence of phosphorus and does not at all interfere with the acceptance of the original hypothesis of valence. So, too, in all similar cases. Nitrogen is really trivalent, but, owing to the formation of molecular compounds, it appears oftentimes to be quinquivalent. By a generous application of this principle, there is no difficulty in accounting for the anomalous cases, and our hypothesis of valence may still be retained, unless it can be shown that there are facts, not yet considered, which do not harmonize with it.

Difficulties met with.—One difficulty immediately presents

itself. Although the examples above given show that there are compounds which seem to differ from true chemical compounds to a sufficient extent to justify us in assuming that they belong to another class of compounds, still there are cases in which there is no ground whatever for making this assumption, and which, nevertheless, show plainly that one and the same element may be at one time trivalent at another quinquivalent, unless we make the above assumption without ground. The compound $POCl_3$, for instance, is not decomposed when converted into the form of vapor, and we have just as much right to consider it a true chemical compound as we have to consider PCl_3 as such. But, in $\overset{\text{v}}{P}\overset{\text{iii}}{O}Cl_3$, phosphorus is apparently quinquivalent, while in PCl_3 it is trivalent. Evidently, here our only ground for considering $POCl_3$ a molecular compound is the fact that its existence cannot be explained by the original hypothesis of valence, unless, indeed we conceive it to be represented by the formula



as some have done. This is dangerous reasoning, and, if we follow it, we shall soon be in serious difficulties. We saw above that the ammonium salts can be explained only on the supposition that the nitrogen in them is quinquivalent, unless we suppose them to be molecular compounds. Plainly, it would be next to absurd to make this supposition, as they have all the characteristics of true chemical compounds, and, if we can assume that they are only molecular compounds, in order to suit our purpose, then we are at liberty to make the same assumption in regard to almost any compound in the field of chemistry.

Experiments showing that Nitrogen may be both Trivalent and Quinquivalent.—Again, an experiment has been performed which appears to show that ammonium chloride NH_4Cl, and analogous compounds of nitrogen, are true atomic compounds. If NH_4Cl is a molecular compound, then, as was explained above, two forces are concerned in the formation of its molecule.

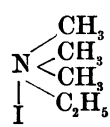
1st. A force holding together the nitrogen atom and three hydrogen atoms forming the molecule NH_3; and the hydrogen atom and chlorine atom forming the molecule HCl.

2d. A force holding together the molecule NH_3 and the molecule HCl.

If these two forces are distinct in character, the resulting molecule might be represented by the formula (NH_3 + HCl). Suppose now we add together two other molecules such that, taken together, their constituent atoms are the same in number and quantity as those contained in the compound (NH_3+HCl). Then the resulting compound ought not to be identical with that obtained in the former case. If these new molecules are, for instance, NH_2Cl and H_2, then the compound will be (NH_2Cl+HH), and this should not be identical with (NH_3+HCl), although its composition is exactly the same.

This principle has been tested, not, indeed, with the molecules employed in the above explanation, but with others analogous to them. Instead of NH_3 the analogous compound, $N(CH_3)_3$, was taken, and this was united with (C_2H_5)I. Thus, a compound was obtained which, if it be molecular, may be represented by the formula ($N(CH_3)_3$ + C_2H_5I). Again, the compound $N(CH_3)_2C_2H_5$ was taken and this was united with CH_3I, yielding a compound which, as in the former case, may be represented by the formula ($N(CH_3)_2C_2H_5$+(CH_3)I). Now these two new compounds ought not to be identical, if they are molecular and not atomic. On comparing them, however, they were found to be in every respect identical.

From this experiment it is concluded that the compounds studied are atomic compounds, and that in them nitrogen is quinquivalent. Each group (CH_3), (C_2H_5), and the element I being held by the same kind of force, the identity of the resulting compounds is readily understood. We have in each



As was stated in a previous chapter, the compound PCl_5 can be converted into vapor under certain circumstances, viz., in the presence of the vapor PCl_3. From this it is concluded that the compound PCl_5 is a true chemical or atomic compound; and, hence, further, that the phosphorus atom contained in it is quinquivalent.

The Distinction between Atomic and Molecular Compounds

unnecessary as far as the Hypothesis of Valence is concerned. —We recognize thus that nitrogen and phosphorus act in some compounds as trivalent, in other compounds as quinquivalent, elements. If we acknowledge this, however, then there is no necessity for assuming the existence of molecular compounds for the purpose of explaining anomalies in the valence of elements. It is very probable, indeed, that in the so-called double compounds, in which we have two or more salts combined with each other, as well as in the salts containing water of crystallization, we have true examples of molecular compounds, in the sense in which this expression has been used in the present article; but it is evident that, as soon as we admit the possibility of one and the same element being either univalent or bivalent, it is no longer necessary to assume the existence of these molecular compounds. We hence leave the study of these peculiar and interesting compounds for the future, and continue the discussion of valence.

Saturated and Unsaturated Compounds.— As soon as the quinquivalence of nitrogen was established, a new explanation was offered concerning the nature of nitrogen compounds. Only those compounds in which the nitrogen is quinquivalent were looked upon as complete. Those in which the nitrogen is trivalent were looked upon as incomplete. For the expressions complete and incomplete, the expressions saturated and unsaturated were employed. The atom of nitrogen having the power to hold in combination five univalent elements or groups is *saturated* when all of its powers are employed, as in the compound NH_4Cl; it is *unsaturated* when only a part of its powers are employed, as in the compound NH_3. The power of the nitrogen atom was expressed by saying that it possesses five *affinities* or *bonds*. In the saturated compound all of these affinities are employed, whereas in the unsaturated compound only a part of them are employed.

To explain the fact that ammonium chloride, NH_4Cl, is readily decomposed by heat, yielding NH_3 and HCl, it was further supposed that of the five affinities of the nitrogen atom two are weaker than the other three. Hence, in a saturated nitrogen compound, two atoms or groups are held less strongly than the other three, and are given off more readily. This same explanation would account for the decomposition of phosphorus chloride, PCl_5, into

PCl_3 and Cl_2, and the other similar decompositions to which reference has already been made. The experiment described above, however, which proved the identity of the compounds—$(N(CH_3)_3+C_2H_5I)$ and $N(CH_3)_2(C_2H_5)$—CH_3I—proved also that the affinities of the nitrogen atom are all of the same kind, and hence we cannot admit that two of the affinities are weaker than the other three. While further, phosphorus chloride, PCl_5 is readily decomposed by heat, in accordance with the supposition that two of the affinities of the phosphorus atom are weaker than the other three, yet, on the other hand, the compound $POCl_3$ gives no evidence of this difference of the affinities. It can also easily be shown that it is not necessary to assume this difference in order to explain the decomposition of phosphorus chloride, PCl_5, and ammonium chloride, NH_4Cl. We may, for instance, suppose that the five affinities of the nitrogen atom, or the phosphorus atom, are all exactly equal in power at the outset. Should three of these affinities, however, become saturated, it seems possible that the presence of the saturating atoms or groups may influence the power of the remaining unsaturated affinities in such a way as to make them weaker than they were at first.

There is in fact at present no good reason for supposing that different parts of atoms exert different kinds of attractive influence. It seems more rational to suppose that, in phosphorus trichloride, for example, all three of the chlorine atoms are influenced in exactly the same way by the phosphorus, and that the whole atom of phosphorus is brought into play. Further, that under certain circumstances the same power of the phosphorus may be distributed uniformly among five chlorine atoms, but that then the compound is less stable than the simpler one. On heating up the less stable compound it loses two chlorine atoms, and the more stable one is formed.

With the evidence before us, it seems that we are justified in abandoning the view that the affinities of the nitrogen atom and similar quinquivalent atoms differ from each other in the strength of the attraction which they exert towards other atoms. It remains then yet to explain, by the aid of some other hypothesis, the ready decomposition of ammonium chloride and phosphorus chloride.

Double Linkage.—To account for the existence of unsaturated compounds, some chemists have supposed that two

affinities of the same atom might in some way act upon each other, causing saturation. The compound in which such a combination exists is then a complete compound, not possessing free affinities. In them, however, the mutual saturation of like affinities can be easily overcome, and then other atoms can be held in combination. This was supposed to be rendered probable by the fact that the number of affinities which are considered as free in unsaturated compounds is always, with very few exceptions, an even number. This would necessarily be the case if the above assumption were true. The idea of double linkage between two atoms of the same kind has perhaps been of service in some cases, but it remains still to be shown whether there is a sufficient basis of facts for it to rest upon.

Variable Valence.—We have already seen that nitrogen and phosphorus act in some compounds as though they are trivalent; in others, as though they are quinquivalent. On examining the compounds of other elements, as we have examined those of nitrogen and phosphorus, we find that some of these also appear at times to have one valence, and at other times another valence. As a consequence of such observations, the hypothesis of valence as first stated in its simplest form was changed, and the change has been accepted by some. Instead of supposing the valence of an atom to be a constant property determined by the nature of the atom, just as the weight and many other properties are necessarily connected with the atom and are constant, it was supposed that the valence could change according to circumstances. These circumstances might be of various kinds, but prominent among them is the temperature. Accordingly, in some of their compounds, nitrogen and phosphorus are trivalent, and in others quinquivalent. Inasmuch as the ammonium compounds, in which the nitrogen is quinquivalent, are decomposed by heat, yielding ammonia, in which the nitrogen is trivalent, and as, further, phosphorus pentachloride, in which the phosphorus is quinquivalent, is decomposed by heat, yielding phosphorus trichloride, in which the phosphorus is trivalent, the conclusion was drawn that, at lower temperatures, the valence of these elements is greater, and that the valence decreases with an increase of temperature. There can be no doubt that the temperature does exert an

influence upon the valence of the elements, and that the tendency of an elevation of temperature is to decrease the valence, but, as yet, we do not know the law governing these changes, and until we do, it will be impossible to reach satisfactory conclusions in regard to the property which in a vague sort of way we call valence.

From the first extreme view, according to which the valence is fixed for every element, some chemists flew to the other extreme, and suggested that the valence of all elements is not only variable, but that it varies between wide limits. The same element may be univalent, trivalent, quinquivalent, heptavalent, etc. Another may be bivalent, quadrivalent, hexavalent, etc. All the elements are divided into two classes, called *artiads* and *perissads*. The members of the former class may have any valence represented by an even number, as 2, 4, 6, 8, etc. Those of the latter class may have any valence represented by an uneven number, as 1, 3, 5, 7, etc. There is, to be sure, a prevailing tendency on the part of each element to act with some particular valence, but, nevertheless, as occasion demands, new powers may be called into requisition, or some of those which usually exhibit themselves may disappear. This extreme view did not at any time meet with much favor, and, at present, very few, if any, uphold it.

Relative Valence.—Würtz has employed the term valence in a sense differing entirely from that in which we have thus far understood it, and in which it has been used by most writers. By it he means the power which an atom actually exhibits in any given compound, not the absolute power of the atom to hold other atoms in combination. He says: "We think that the important thing is not to fix the atomicity which each element possesses absolutely, but that which it manifests in a given compound." He then points out the difficulties in the way of determining the absolute atomicity of an element, and abandons the attempt to accomplish the determination. Further, he calls attention to the fact that the force with which one atom attracts another depends upon the properties of both atoms, and cannot be measured absolutely by the force of one of the atoms. So, also, he conceives that an atom may be trivalent towards one kind of atoms and quinquivalent towards another. He says, in this connection: "The property which phosphorus possesses

of uniting with five atoms of chlorine depends, without doubt, upon a particular condition of the atoms, their form, structure, volume, movements. This condition, which is unknown to us, is invariable for phosphorus, and if one atom of phosphorus can unite with five atoms of chlorine, while it can only unite with three atoms of hydrogen; if it is quinquivalent as regards chlorine, and trivalent as regards hydrogen, we ought to seek for the reason of these differences, not only in the atoms of phosphorus, but also further in those of chlorine and of hydrogen."

The proposition, then, is to abandon the idea of valence, as it has been defined, and to substitute for it a variable idea. The valence of an atom is thus not a fixed property of the atom determining the nature of the compound which this atom forms with others, but, these compounds having been formed by virtue of unknown properties of atoms, the valence is that particular combining power which the atom happens to exhibit. The difference between these two conceptions of valence are as great as that between the conception of atomic weight and equivalent.

There are undoubtedly strong reasons for the step proposed by Würtz. The difficulties in the way of determining the absolute valence of an element are fully as great as they are represented to be by Würtz, and there can be little doubt that the valence of an element depends to some extent upon the element with which it is combined, but our knowledge of this order of facts is too limited to warrant us in making positive statements about them.

From a consideration of all the facts it appears then that the property of valence is one of great importance, and that it exerts a controlling influence in all cases of chemical action. It is, however, to some extent, a variable property, the variations being due to several causes, among which are undoubtedly the temperature and the nature of the element or elements with which the one we may be considering is combined. When investigation shall have proceeded far enough to enable us better to understand this property than we do at present, we shall probably find, as has been held throughout this discussion, that the valence of the atom determines in every case the complexity of the molecule; and that, knowing the valence and nature of the atoms entering into combination, we shall be able to foretell the composition of the molecule. Because we cannot do this at

present, it does not appear wise to abandon the idea completely.

It will be pointed out, under the head of the Constitution of Chemical Compounds, that the hypothesis of valence finds its principal use in connection with compounds of carbon, and particularly for the purpose of expressing the relations between the carbon, oxygen, and hydrogen contained in them. Now, although carbon does sometimes act as a quadrivalent and sometimes as a bivalent element, it is possible in many cases to determine by chemical methods whether we have carbon present in the bivalent condition or not, so that in making use of the hypothesis for the purpose of expressing the constitution of carbon compounds we encounter very little difficulty in the great majority of cases. The application of the hypothesis to the explanation of the so-called inorganic compounds is of doubtful value at the present stage of its development.

Owing to the variations in the valence of the elements it is, of course, very difficult to classify them with reference to this property. While acknowledging the variations, however, it must be borne in mind that each element has a tendency to act with some particular valence. Thus, the tendency of carbon is to act as a quadrivalent element. Apparently the extent of the variation is limited. Thus, nitrogen and phosphorus appear either as quinquivalent or trivalent elements—not as univalent or heptavalent.

The subjoined table fairly represents the state of our knowledge on the subject at present. It is, no doubt, exceedingly imperfect. Investigations, at present being carried on, are tending to perfect it. We are far from a complete understanding of the subject, so that any discussion of it must necessarily be very imperfect. In the above, the attempt has been made to show, as nearly as possible, where we stand with reference to it, to show that some of the hypotheses which have been proposed concerning this property have not sufficient foundation to warrant us in accepting them, and to reduce the hypotheses back to the simplest form, to determine which assumptions are justifiable and which are not. This is all we can do at present.

I. *Univalent Elements.*

Hydrogen,	H
Chlorine,	Cl
Bromine,	Br
Iodine,	I
Fluorine,	Fl
Potassium,	K
Sodium,	Na
Cæsium,	Cs
Rubidium,	Rb
Lithium,	Li

II. *Bivalent Elements.*

Oxygen,	O
Sulphur,	S
Selenium,	Se
Tellurium,	Te
Barium,	Ba
Strontium,	Sr
Calcium,	Ca
Magnesium,	Mg
Glucinum,	Gl
Zinc,	Zn
Cadmium,	Cd
Copper,	Cu
Mercury,	Hg

III. *Quadrivalent Elements.*

Silicon,	Si
Titanium,	Ti
Zirconium,	Zr
Thorium,	Th
Yttrium,	Y
Cerium,	Ce
Lanthanum,	La
Didymium,	Di
Gallium,	Ga

IV. *Quinquivalent Element.*

Niobium,	Nb

V. *Univalent and Trivalent Elements.*

Gold,	Au
Indium,	In

VI. *Bi- and Quadrivalent Elements.*

Carbon,	C
Tin,	Sn
Lead,	Pb
Nickel,	Ni
Cobalt,	Co
Iron,	Fe
Manganese,	Mn
Chromium,	Cr
Aluminium,	Al
Platinum,	Pt
Iridium,	Ir
Palladium,	Pd
Osmium,	Os
Rhodium,	Rh
Ruthenium,	Ru

VII. *Tri- and Quinquivalent Elements.*

Antimony,	Sb
Arsenic,	As
Phosphorus,	P
Nitrogen,	N
Tantalum,	Ta
Vanadium,	V
Bismuth,	Bi

VIII. *Sexivalent Element.*

Tungsten,	W

IX. *Quadrivalent and Sexivalent Element.*

Uranium.

PART SECOND.

CONSTITUTION OR STRUCTURE OF CHEMICAL COMPOUNDS.

I.

GENERAL CONSIDERATIONS.

DEFINITION OF CONSTITUTION, ETC.

Definition, etc.—If all chemical compounds could be converted into vapor and the truth of Avogadro's hypothesis could be established beyond reasonable doubt, it would be possible to determine molecular formulas of these compounds. The steps involved in determining the formula of a compound are these:

1. The compound must be analyzed: the percentages of its constituents must be determined. This involves no hypothesis. If, in expressing the results of the analysis, we say the compound contains a certain percentage of carbon, a certain percentage of oxygen, and a certain percentage of hydrogen, we simply state facts.

2. If, however, we express the results by a chemical formula we then make use of some hypothesis. At the present day the hypothesis involved in the simplest chemical formulas, such as HCl, H_2O, H_3N, etc., are, in the first place, the atomic hypothesis, and, in the second place, Avogadro's hypothesis. In writing these formulas we mean to express the composition of a molecule of each compound. In many cases we cannot determine the specific gravity of the vapor of the compounds, and we then have no means for determining the molecular weight. Thus, take sodium sulphate. We write the formula Na_2SO_4 for this compound, but we have no means of judging whether that formula really expresses the true molecular weight of the compound or not.

It expresses the percentage composition, and, if we accept the atomic weights as determined by the rules of Avogadro and of Dulong and Petit, the formula given is the simplest one possible. This is the only reason for adopting it. As far as reason is concerned we are just as much justified in writing it $Na_4S_2O_8$ or $Na_6S_3O_{12}$, and, indeed, there are some facts known to us which seem to indicate that these more complex formulas are really nearer the truth than the simple one now in use. This, however, is not a matter of much importance in the present stage of chemistry. For most purposes the formula Na_2SO_4 is quite satisfactory.

The formulas which simply express the percentage composition of molecules are commonly known as *empirical formulas*. Can anything else be fairly represented by a chemical formula? It will be observed that the empirical formulas have nothing whatever to do with the conduct of the compounds they represent. On studying the action of chemical compounds upon each other we gain a mass of knowledge which it is very desirable to express in a concise form. We find that certain compounds resemble each other very closely in their conduct, though they may differ markedly in composition; we learn that the presence of certain constituents in a compound causes it to act in a particular way; we learn that, although the number of compounds is unlimited, the number of classes of compounds is comparatively small, etc., etc. If formulas can be devised that will aid us in expressing intelligibly the results of investigation, they can lay claim to notice.

From the earliest periods of chemistry formulas of this kind have been used. Without going back to the beginning it will be instructive to recall the general character of these formulas from the time of Lavoisier.

This chemist, as is well known, paid particular attention to the phenomena of combustion. He regarded all compounds as made up of a combustible and an incombustible part. In his formulas he separated these two parts.

When the electro-chemical theory held sway every compound was supposed to consist of an electro-positive and an electro-negative constituent. Hence every formula consisted of two parts. To determine the formula according to this theory a compound was subjected to the decomposing influence of the electric current. It was thus separated into two parts, and these parts were written separately in the formula.

The old formulas for salts, such as $NaO.SO_3$, $KO.NO_5$, etc., which we see even at the present day, particularly in works on mineralogy and analytical chemistry, have come down to us from the period of the electro-chemical theory. They involve much more speculation than the formulas now in use, and that too of a kind which has been shown to be unfounded.

The next idea which we find playing an important part in the construction of chemical formulas is that used by Liebig. This chemist, and many others after him, effected the decomposition of compounds and noticed what products were obtained. In writing the formula of the original compound they then indicated in it the presence of the products they had obtained from it.

After this came the idea of types, which was developed by Dumas and became known as the "theory of types." According to this "theory" all chemical compounds may be referred to a few fundamental compounds or types. All compounds belonging to the same type are constructed on the same plan. The types which have been proposed up to the present time are:

I.	II.	III.	IV.
HCl,	H_2O,	H_3N,	H_4C.
Hydrochloric Acid.	Water.	Ammonia.	Marsh Gas.

There is something distinctive in each of these compounds and the traits which characterize it are met with in the compounds belonging to the same type. On attempting to make use of the type theory for the purpose of classifying compounds serious difficulties are met with, mainly for the reason that many bodies belong, not to one type, but to several.

The introduction of the idea of "mixed types" did much to overcome these difficulties, but still without enlargement the idea of types could not furnish a sufficient basis for formulas which should express the principal facts known regarding chemical compounds. The "theory" was, however, of great importance, as it furnished a rational means for the classification of chemical compounds, and directed attention to fundamental differences between the elements.

An examination of the types shows that the elements chlorine, oxygen, nitrogen, and carbon differ from each other in their power of holding hydrogen in combination,

and leads to the conclusion that the reason for the existence of these types must be looked for in the nature of the elements of which they are composed. This brings us at once to the valence hypothesis, which has already been discussed. At the present time, chemical formulas are based upon the atomic hypothesis, the hypothesis of Avogadro, and the valence hypothesis. As there is a great deal of misunderstanding in regard to these formulas, as by some they are overvalued, and by others undervalued, a brief statement, concerning their exact significance, is desirable.

It cannot be denied that we are now in a period of chemistry which may fairly be called one of *formula worship*. By weaker minds more value is attached to a formula than to that which it is intended to represent. In consequence of this truth it has happened that a large number of chemists have regarded the determination of a formula for a compound as the great object to be accomplished, and forgotten that what we ought to know, and what is of vastly greater importance for the science, is the chemical conduct of the compound. If, knowing this, we can represent it by means of a formula, not only are we justified in doing so, but the formula becomes an efficient aid in dealing with the compound. Formulas have been proposed for nearly all compounds known. Some of these, indeed many of them, are valuable, but many are not. Before considering the means at our command for deciding whether a formula is valuable or not, a few words in regard to the general methods in use for determining formulas will be necessary.

After the empirical formula, as above defined, has been determined, the next thing to be done is to study the compound in every way possible, both by chemical methods and by physical methods. We must learn exactly how it conducts itself under all circumstances which we can control. When this study is finished, we shall have in our possession a mass of facts. We shall know much more than the composition, and we ought to be able to express much more than the composition by our formula. It is, however, by no means necessary that these facts should be expressed in the formula, any more than it is necessary that the composition should be expressed in a formula. Now, how can we express anything in regard to the conduct of a compound by means of a formula? As a simple example, acetic acid may be taken. The empirical formula is easily found

to be $C_2H_4O_2$.* We find that exactly one-fourth of the hydrogen contained in the compound can easily be replaced by metals. Thus, with potassium hydroxide or carbonate we get $C_2H_3O.K$. We cannot replace any more of the hydrogen by metals, so that we are justified in concluding that one of the four parts of hydrogen, represented in the empirical formula, differs from the other three. We may, hence, write the formula $C_2H_3O_2.H$, which emphasizes the difference found by experiment.

Further, when acetic acid is treated with phosphorus trichloride, it is converted into a compound of the formula, C_2H_3OCl; that is, the acid loses one part of hydrogen and one part of oxygen, and takes up in place of them one part of chlorine. When the chlorine compound is treated with water, acetic acid is regenerated, and hydrochloric acid is formed:

$$C_2H_3OCl + H_2O = C_2H_3O_2.H + HCl.$$

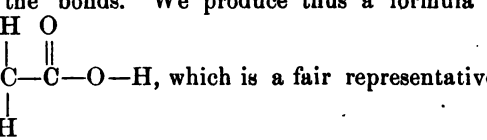
This reaction makes it appear probable that, in acetic acid, one of the oxygen atoms is intimately associated with a hydrogen atom. The two leave the acid together, and enter it together. We may express this fact by the formula $C_2H_3O.OH$. The chlorine compound, formed by treatment with phosphorus trichloride, contains no hydrogen replaceable by metals, so that it appears extremely probable that the hydrogen, which is represented by itself in the formula $C_2H_3O_2.H$, is the same as that represented as associated with oxygen in the formula $C_2H_3O.OH$. In a similar way it can be shown that the second oxygen is probably associated with carbon in the same way as it is in carbon monoxide. We, hence write $CO.CH_3.OH$. This formula expresses the result of reactions studied, and it may, hence, be called a *reaction formula*. We can supplement the knowledge gained by the reactions above referred to by making acetic acid from simpler substances, that is, by the process of synthesis. Thus, for example, we may start from marsh-gas, CH_4, and carbonyl chloride, $COCl_2$. These substances, or similar substances, act upon each other as represented thus:

$$CH_4 + COCl_2 = CH_3.COCl + HCl.$$

* If, at this stage, there is the slightest doubt in the student's mind in regard to the exact basis upon which this formula rests, he should read the first part of the book over as frequently as may be necessary to cause the disappearance of the doubt. Nothing can be clear in chemistry until this doubt has entirely disappeared.

If the product $CH_3.COCl$ is found to be identical with that above mentioned as resulting from the action of phosphorus trichloride or acetic acid, and which was represented by the formula C_2H_3OCl, then, taking the facts above described into consideration, we are led to the formula $CH_3.CO.OH$ for acetic acid. This formula, as far as it is based upon the synthesis of acetic acid, may be called a *synthesis formula.*

The *reaction formula* and the *synthesis formula* go hand in hand. Both express facts established, and are of value in enabling us to deal with the facts. Most of that, which is of value in the formulas in common use, is independent of the hypothesis of valence. The formulas of acetic acid above given have nothing to do with this hypothesis, and if now we bring in the hypothesis to aid us, it is, at least, questionable whether we gain anything. All we can accomplish by means of it is to account for the employment of the hypothetical affinities or bonds of the elements. We must start with the assumption that carbon is quadrivalent, oxygen bivalent, and hydrogen univalent, and then bearing in mind the reactions above described, we may arrange the formula $CH_3.CO.OH$ in such a way as to satisfy the bonds. We produce thus a formula like this,



which is a fair representative of what are known as *constitutional* or *structural formulas.*

By a constitutional or structural formula, then, we mean one which expresses: 1st. The decompositions of the compound; 2d. The syntheses of the compound; and 3d. The relations existing between the parts of the compound, in terms of the valence hypothesis.

It must be distinctly stated that we cannot use the valence hypothesis, except to supplement the reaction and synthesis formulas. We are not justified in going beyond the facts established. Here lies the danger in the use of structural formulas. Their wholesale use to express something about which we know absolutely nothing has tended to bring them into disrepute, but this fact should not cause their entire rejection, for there is undoubtedly much of value in them when rightly used.

In the following parts of this book, the attempt will be made to show upon what basis the structural formulas of the principal chemical compounds rest. In using the formulas the student should accustom himself to ask in every case exactly what is meant. Above all things, he should not be satisfied because all the hypothetical bonds are satisfied.

Linkage of Atoms.—It was stated above that "most of that which is of value in the formulas in common use is independent of the hypothesis of valence." There is, however, an hypothesis underlying the conception of valence, which is necessarily involved in all our structural formulas, and that is the hypothesis of the linkage of atoms.

It is plain that, considering any complex compound, say, acetic acid, $C_2H_4O_2$, there are, at least, two views possible in regard to the relations of the constituents. Either these constituents, or, to speak in terms of the atomic hypothesis, these atoms, are all united, each one with every other one, or they are not all united thus. We have excellent reasons for believing that the latter is the correct view; that the atoms are united or linked together in forms which may be called chains with branches. We are forced to this view by an overwhelming array of facts, prominent among which is the existence of the so-called homologous series. The relations between the members of these series find their simplest explanation in the assumption that the carbon atoms are linked together.

We have the series, CH_4, C_2H_6, C_3H_8, C_4H_{10}, etc., the members of which very closely resemble each other. The second member, C_2H_6, may be made from the first, by introducing chlorine into the latter, the product CH_3Cl being formed. Now, if, under proper circumstances, this substance be treated with sodium, the chlorine is extracted, and the substance C_2H_6 is formed. The simplest explanation of these reactions is this: The carbon atom in methane, CH_4, holds the four hydrogen atoms, and can do nothing more. Chlorine cannot be added to this compound, but it can drive out hydrogen, and occupy the place thus made vacant. Now, if the chlorine be removed, union may be effected between two carbon atoms, and, according to this, the resulting compound must be represented by the formula $H_3C—CH_3$, which indicates that the carbon atoms are

linked together, and that the hydrogen atoms are in combination with the carbon atoms. It may safely be said that all the facts known to us speak for the correctness of this view.

To be sure, the hypothesis of valence is also involved in this explanation, but the main point to be noticed here is, that we are forced to the conclusion that the atoms are linked together, that there is some definite arrangement between them.

Having been forced to this view, the problem presents itself in the case of every compound to determine how the atoms are linked together. If we can do this, we can determine the constitution of the compound, and, if the determination is properly made, the result is almost entirely independent of the hypothesis of valence. As already pointed out, we can determine these relations only by means of experiment. The determination is never absolute. All that we can say is that the compound conducts itself as if hydrogen and oxygen were united, or *as if* two carbon atoms were linked together, and we then make use of a formula to recall this to mind. Such relations, established by actual experiment, are about all we can express in the formula, and, if we then go beyond them, and distribute the "bonds" so that all are satisfied, we are dealing with pure hypothesis, and are not gaining any additional insight into the nature of the compound.

If the question be asked, what is the meaning of the expression "linkage of atoms?" the only answer that can be properly given is, that it is simply a convenient phrase to indicate the condition which we believe to exist between the smallest parts of all chemical compounds. As to its character, we know absolutely nothing. If we could tell exactly what relation the smallest particle of chlorine bears to that of hydrogen in hydrochloric acid, we could tell what is meant by "linkage of atoms." All that we know is that the chlorine and hydrogen do act upon each other in some wonderful way, that they both disappear as such, and that we get something in which both are present. We believe that the act of union takes place between the atoms of the elements, and we represent the compound by the formula HCl, or H.Cl, or H—Cl. It is not at all probable that a firm union exists between the two parts, in such a way as to render the parts of the molecule immovable with refer-

ence to each other. Much more likely is it that, after the union, the atoms perform some kind of motion with reference to each other, according to the laws of atomic motion yet to be discovered. For our present purpose, it is sufficient to know that, in whatever manner the union takes place, the chemical activity of the atoms ceases in consequence.

In writing a structural formula, we do not commit ourselves with regard to the character of the union between the parts, nor with regard to the position of the parts in space. All that we can attempt to do at present is to indicate the probable relation between the parts. Thus, by the formula, $H_3C—C—N$, we mean that the reactions and methods of formation of the compound represented lead to the conclusion that the two carbon atoms are closely related or linked together, while the three hydrogen atoms are linked to one of the carbon atoms, and the nitrogen to the other. The reactions of the substance and the methods of formation lead us to believe that these relations exist in it. If we go farther, and represent the substance by the formula $H_3C—C\equiv N$, we are then simply applying the hypothesis of valence, and we really gain nothing. We know nothing about the relation existing between the carbon and nitrogen, though the above formula seems to indicate that the relation is a firmer one than that expressed by the simple line as C—N.

The formulas in use for the various classes of compounds known to us will now be considered, more particularly with the object of showing the connection which exists between the facts and the formulas. After the classes have been considered, the principal compounds of each class will be taken up and treated in a similar manner. In this section, the proofs made use of will be entirely of a chemical character. In a subsequent section, the question of the relations between physical properties and constitution will be briefly considered.

Classes of Compounds.

Chemical compounds may be most conveniently classified according to their chemical properties. No system of classification which has been proposed, up to the present, can, in any sense, be called perfect, and yet the system now in

most common use is convenient, and has a fair foundation of facts.

If we examine the compound which has the formula HCl, hydrochloric acid, and the compound which has the formula KOH, potassium hydroxide, we find that the two compounds differ very markedly from each other. The former has a taste which we call sour, the latter has the taste of lye, or an alkaline taste. The former will turn the color of many organic substances, while the latter will undo the work done by the former, restoring the original color. In whatever way we may consider these two compounds, we shall find that they have opposite or complementary properties. They are both chemically active substances, capable of producing marked changes in large numbers of other compounds. If they are brought together, they neutralize each other, that is to say, they destroy each other's active properties, and give rise to the formation of a new compound, differing entirely from the two. The two compounds, hydrochloric acid, HCl, and potassium hydroxide, KOH, are representatives of two great classes of compounds known as *acids* and *bases*. Many of the members of these two classes possess just as marked properties as do the two which have been mentioned, and for these the classification into acids and bases is rational and simple. But there are, further, some compounds which appear to possess the characteristics of both classes to a certain extent, and of neither class very markedly. They act like acids towards some bases, and like bases towards some acids. The role which they play depends upon the character of the substances with which they are brought in contact.

Acids.—The properties which characterize acids, are the following:

1. They have an acid or sour taste.
2. They change blue litmus red.
3. They act upon metals, hydrogen being evolved, and its place being taken by the metals, as, for instance:

$$\underset{\text{Hydrochloric acid.}}{2(HCl)} + Zn = \underset{\text{Zinc chloride.}}{ZnCl_2} + 2H$$

$$\underset{\text{Sulphuric acid.}}{H_2SO_4} + Mn = \underset{\text{Manganese sulphate.}}{MnSO_4} + 2H$$

4. They act upon metallic hydroxides, forming neutral substances and water, as follows:

$$\underset{\text{Hydrochloric acid.}}{HCl} + \underset{\text{Potassium hydroxide.}}{KOH} = \underset{\text{Potassium chloride.}}{KCl} + H_2O$$

$$\underset{\text{Nitric acid.}}{HNO_3} + \underset{\text{Sodium hydroxide.}}{NaOH} = \underset{\text{Sodium nitrate.}}{NaNO_3} + H_2O$$

$$\underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Calcium hydroxide.}}{Ca(OH)_2} = \underset{\text{Calcium sulphate.}}{CaSO_4} + 2H_2O$$

Hydrogen Acids.—All acids contain hydrogen. They may consist of hydrogen and only one other element, or of hydrogen and a group of other elements of greater or less complexity. The constitution of those acids which consist of hydrogen and only one other element, is, of course, very simple and readily understood. There are but few examples of this kind, among which are hydrochloric acid, HCl, hydrobromic acid, HBr, sulphydric acid, H_2S, etc. According to our conceptions of the nature of chemical constitution, compounds of the above formulas can have only one constitution.

It is a noticeable fact that acids of this first and simplest class never contain more than two atoms of hydrogen in the molecule, or, that no element with a higher valence than two forms these simple acids.

Hydroxyl Acids.—By far the greater number of acids belong to the second class mentioned. They consist of hydrogen and a group of greater or less complexity, as, for instance, $H(NO_3)$, nitric acid; $H(ClO_3)$, chloric acid; $H_2(SO_4)$, sulphuric acid, etc. In nearly all acids of this kind, oxygen is one of the constituents of the group, with which the hydrogen is combined.

The hydrogen in these compounds is the changeable constituent. It is readily given up, and metals and groups are taken up in its place. The first question that suggests itself, in considering the constitution of acids, is this: In what manner is the hydrogen in them held in combination? It is believed that investigations, thus far made, justify the answer that the hydrogen in these acids is almost always in combination* with oxygen, and, in a very few

* The expression "in combination" is here used, and will be used hereafter, in the sense in which it has already been explained. By it is meant simply that the compounds conduct themselves *as if* the hydrogen and oxygen were in combination—and that is all we know about the matter.

cases, with that element which is so similar to oxygen, viz., sulphur. The proofs for this statement cannot always be given. In the cases of many acids there exist no independent proofs that, in these, the hydrogen is combined with oxygen. On the other hand, there are so many acids in which it can be satisfactorily shown that the hydrogen is thus combined that the above answer seems to be justified. We accordingly write the formulas of acids in such a way as to indicate the fact of union between oxygen and hydrogen thus:

$(HO)NO_2$	$(HO)ClO_2$	$(HO)_2SO_2$
Nitric acid.	Chloric acid.	Sulphuric acid.

Or, these same formulas may be made still more definite by writing them as follows:

$$H-O-NO_2, \quad H-O-ClO_2, \quad \begin{matrix} H-O \\ \diagdown \\ SO_2 \\ \diagup \\ H-O \end{matrix}.$$

Proofs.—Under certain circumstances, an atom of oxygen and an atom of hydrogen may be removed from an acid containing oxygen, and one atom of chlorine then enters into the place occupied by the displaced atoms, and is held in combination. Now, the simplest conclusion we can draw is that the oxygen and hydrogen were present in the compound as a univalent group, viz., as (OH), or hydroxyl.

We have the following instances:

$SO_2(OH)_2$ yields the compounds

$SO_2(Cl)(OH)$	and	SO_2Cl_2.
Sulphuryl oxichloride.		Sulphuryl chloride.
$PO(OH)_3$	yields	$POCl_3$.
Phosphoric acid.		Phosphorus oxichloride.
$C_2H_3O(OH)$	yields	C_2H_3O-Cl, etc.
Acetic acid.		Acetyl chloride.

Another reaction, which shows plainly that in these acids hydrogen is intimately associated with oxygen, is that by

which the group NH_2 is introduced into them in the place of an atom of oxygen and an atom of hydrogen. The fact that the elements, oxygen and hydrogen, are displaced together indicates a connection between them in the compound.

We have the following instances:

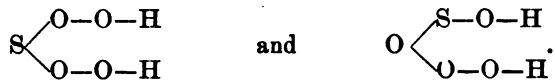
$C_2H_3O(OH)$ Acetic acid.	yields	$C_2H_3O(NH_2)$ Acetamide.
$C_7H_5O(OH)$ Benzoic acid.	yields	$C_7H_5O(NH_2)$ Benzamide.

These, with other general reactions, furnish the proof of the statement above made, that, in most of those acids which contain oxygen, the characteristic hydrogen is in combination with oxygen in the form of hydroxyl (OH). In some few cases, as already mentioned, the oxygen is replaced by sulphur.

Further Experiments necessary in most Cases.—If we accept the statement that hydroxyl is present in oxygen acids, we are prepared to take another step. This hydroxyl may be in combination with only one element or with a group of elements. If it is in combination with only one element, the constitution of the resulting acid is easily understood. For nstance, in the compound ClOH, hypochlorous acid, only ione method of combination suggests itself, viz., Cl—O—H. There are very few examples of this kind.

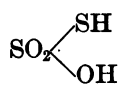
In those acids in which the hydroxyl is in combination with a group, the constitution is determined when, in addition to showing the presence of hydroxyl, the special constitution of the group itself is determined.

In sulphuric acid, for instance, after having determined the presence of two hydroxyl groups, we have the formula $SO_2\langle^{OH}_{OH}$; but this formula only partially expresses the constitution of the acid. It remains to be shown in what manner the atoms are combined in the group SO_2, and also, with what atoms the hydroxyl groups are combined. Under the assumption that both sulphur and oxygen are bivalent elements, the constitution of sulphuric acid may be expressed by two different formulas, viz.:



Special experiments must decide which of these formulas is the correct one, or whether either is correct.

Other Acids.—It has been mentioned that, in some acids, sulphur plays the part which oxygen plays in the hydroxyl acids. In these we have the univalent group (SH). The grounds for assuming the presence of this group in a compound are similar to those which lead to the assumption that the group (OH) is present. The two atoms S and H can both be removed from the compound and be replaced by one univalent atom, as chlorine; and, further, there is a general tendency on the part of these two elements, sulphur and hydrogen, to leave the compound in company. Examples of acids of this kind are



Hyposulphurous acid.

and CN(SH).

Sulphocyanic acid.

Lastly, there is one acid which can be classified under none of the above heads. It contains hydrogen probably in combination with carbon, the latter being at the same time in combination with nitrogen. This is hydrocyanic acid, H—(CN), in which the group CN acts like an element, making the compound analogous to hydrochloric acid, HCl.

Subdivision of Acids.—It will be seen that different acids contain different numbers of hydroxyl-groups in their molecules. An acid which contains only one such group in its molecule has, of course, only one characteristic hydrogen atom. It is called a *monobasic* acid. An acid which contains two such groups in its molecule is a *bibasic* acid. We have, further, *tribasic*, *tetrabasic* acids, etc.

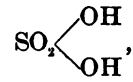
The same distinctions are possible among those acids which consist of hydrogen combined only with an element, and consequently do not contain hydroxyl; but as of these latter acids we have none which contain more than two atoms of hydrogen in the molecule, so we have among them only monobasic and bibasic acids.

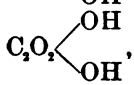
Examples:

Monobasic acids.

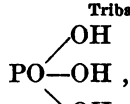
HCl, hydrochloric acid.
$NO_2(OH)$, nitric acid.
$Cl(OH)$, hypochlorous acid.

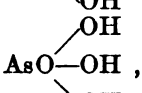
Bibasic acids.


, sulphuric acid.


, oxalic acid.

Tribasic acids.


, phosphoric acid.


, arsenic acid.

Tetrabasic acids.

$P_2O_3(OH)_4$, pyrophosphoric acid.

Bases.—Bases have properties which are the opposite of those possessed by acids. They all contain oxygen and hydrogen, and these elements are combined as hydroxyl, as may be shown in the same way that it was shown for acids. The most striking characteristic of bases is their power to act upon acids, forming neutral substances and water, as is seen in the following reactions:

$$\underset{\text{Potassium hydroxide.}}{KOH} + \underset{\text{Nitric acid.}}{HNO_3} = \underset{\text{Potassium nitrate.}}{KNO_3} + H_2O$$

$$\underset{\text{Calcium hydroxide.}}{Ca(OH)_2} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Calcium sulphate.}}{CaSO_4} + 2H_2O$$

Almost all bases consist of a metal combined with hydroxyl. A few appear to consist of a group of atoms combined with hydroxyl.

According to the valence of the metals with which the hydroxyl is combined, we have bases with one, two, three, etc., hydroxyl groups in the molecule. Examples of these are the following:

$K(OH)$, potassium hydroxide.
$Na(OH)$, sodium hydroxide.
$Ca(OH)_2$, calcium hydroxide.
$Ba(OH)_2$, barium hydroxide.
$Al(OH)_3$, aluminium hydroxide.
$Cr(OH)_3$, chromium hydroxide.
$Ti(OH)_4$, titanium hydroxide.
$Zr(OH)_4$, zirconium hydroxide.

Differences between Acids and Bases.—The difference between acids and bases is dependent upon the nature of the elements or groups with which the hydroxyl is combined. The hydroxyl compounds of those elements which have a markedly metallic character are bases. The hydroxyl compounds of those elements which have a markedly non-metallic character are acids. If we consider the hydroxyl compounds of those elements which are neither markedly metallic nor non-metallic, we find that they sometimes act as acids and sometimes as bases. Thus the compound SbO(OH), antimonyl hydroxide, is a weak base and a weak acid, exhibiting one property or the other, according to the nature of the compound with which it is brought in contact.

Complex Bases.—As above stated, there are a few bases which appear to consist of hydroxyl combined with a group of atoms. Such, for instance, are

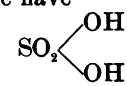
$BiO(OH)$	$UO(OH)$	$TiO(OH)_2$
Bismuthyl hydroxide.	Uranyl hydroxide.	Titanyl hydroxide.

These formulas are based upon the assumption that if one molecule of a base has the power to neutralize one molecule of a monobasic acid, it must contain one hydroxyl group; if it can neutralize two molecules of a monobasic or one of a bibasic acid, it must contain two hydroxyls, etc. Now, bismuthyl hydroxide, or the quantity of substance represented by BiO_2H, has the power to neutralize one molecule of a monobasic acid. It is, as we say, a *mon-acid base*, and contains one hydroxyl. We thus get the formula BiO(OH). We have no means of deciding how the bismuth and oxygen are combined, or whether the hydroxyl is in combination with bismuth or with oxygen. If, however, we assume that bismuth is trivalent, and construct the formula on the basis of the valence hypothesis we have O = Bi—O—H, but that is a mere formula and represents nothing known to us.

Salts.—The neutral substances, to which reference has been made, formed by the action of acids upon bases, are called salts. Salts may be considered either as acids in which the hydrogen has been replaced by a base minus hydroxyl, or as bases in which the hydrogen has been replaced by an acid minus hydroxyl. As the base residues are usu-

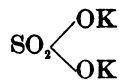
ally simpler than those of the acids, the former view is most commonly held, although the two views are, of course, identical.

It is a simple matter to deduce the constitution of a salt from that of the acid and base or bases from which it is derived. Usually the hydrogen of the acid is replaced by one or more metals, the latter, as is believed, being held in combination by the same force or forces that held the former. Thus we have

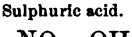


Sulphuric acid.

and

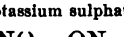


Potassium sulphate.



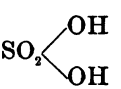
Nitric acid.

and



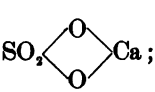
Sodium nitrate.

Or, a bivalent element may enter into an acid, in which case two hydrogen atoms will be replaced, thus:

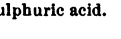


Sulphuric acid.

and

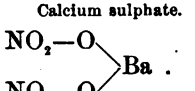


Calcium sulphate.



Nitric acid.

and



Barium nitrate.

Further complications are introduced when trivalent and quadrivalent elements enter into the composition of salts. From what has been said, however, the constitution of these salts will be readily understood.

Complex Salts.—Just as we have a few bases which consist of hydroxyl combined with groups of atoms, so we have salts which may be considered as derived from acids by the replacement of hydrogen by groups of atoms. Thus, a salt obtained from the acid NO_2—OH, and the base UO—OH, probably has the constitution expressed by the formula NO_2—O—UO. Here the hydrogen of the acid is replaced by the group UO, which is univalent.

Anhydrides.—The constituents of water may be abstracted from many acids, and thus a new class of compounds, called

anhydrides, is formed. The most striking characteristic of these compounds is their power to form acids with water, or to form salts by direct union with bases. The following are examples of anhydrides: Sulphuric anhydride, SO_3; nitric anhydride, N_2O_5; phosphoric anhydride, P_2O_5; acetic anhydride $(C_2H_3O)_2O$, etc.

When an anhydride is formed from a monobasic acid, two molecules must combine to furnish the hydrogen for the water. After the abstraction of the water, the two acid residues remain united, through the instrumentality of an atom of oxygen, thus:

$$\left.\begin{matrix} NO_2{-}OH \\ NO_2{-}OH \end{matrix}\right\} - H_2O = \begin{matrix} NO_2 \\ NO_2 \end{matrix}\!\!>\!O ;$$

2 molecules nitric acid. — Nitric anhydride.

$$\left.\begin{matrix} C_2H_3O{-}OH \\ C_2H_3O{-}OH \end{matrix}\right\} - H_2O = \begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\!\!>\!O .$$

2 molecules acetic acid. — Acetic anhydride.

When an anhydride is formed from a bibasic acid, a molecule of water may be given off from a molecule of acid, thus:

$$SO_2\!<\!\begin{matrix} OH \\ OH \end{matrix} - H_2O = SO_3 ;$$

Sulphuric acid. — Sulphuric anhydride.

$$CO\!<\!\begin{matrix} OH \\ OH \end{matrix} - H_2O = CO_2 .$$

Carbonic acid (hypothetical). — Carbonic anhydride.

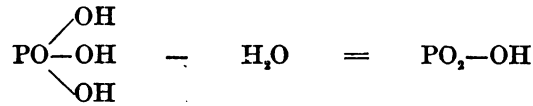
Or, two molecules of a bibasic acid may unite and give off one molecule of water, forming a compound which is, at the same time, an acid and an anhydride, thus:

$$\left.\begin{matrix} SO_2\!<\!\begin{matrix} OH \\ OH \end{matrix} \\ SO_2\!<\!\begin{matrix} OH \\ OH \end{matrix} \end{matrix}\right\} - H_2O = \begin{matrix} SO_2\!<\!OH \\ SO_2\!<\!OH \end{matrix}\!\!>\!O .$$

2 molecules sulphuric acid. — Pyrosulphuric acid.

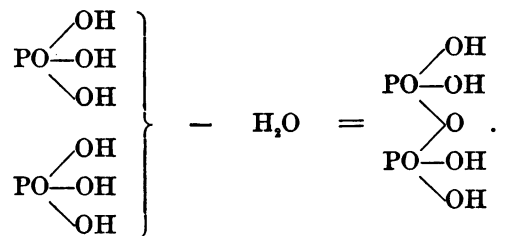
When an anhydride is formed from a tribasic acid, several possibilities present themselves. 1. One molecule of

the acid may lose one molecule of water, a compound being formed which is anhydride and acid, thus:



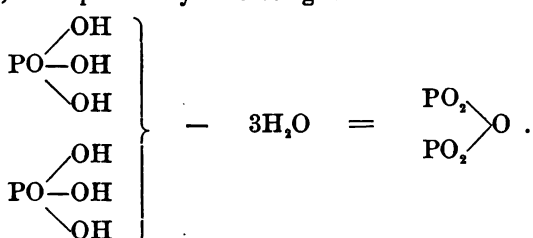
Phosphoric acid. Metaphosphoric acid.

2. Two molecules of the acid may lose one molecule of water, a compound being formed which is a tetrabasic acid, and, at the same time, an anhydride:



2 mol. Phosphoric acid. Pyrophosphoric acid.

3. Two molecules of the acid may lose three molecules of water, a complete anhydride being formed:

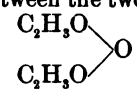


2 mol. Phosphoric acid. Phosphoric anhydride.

By combining a larger number of molecules of the acids and abstracting different numbers of molecules of water, a great variety of anhydrides might be produced, at least theoretically. Not many such complicated products are positively known, however.

From tetrabasic acids and acids with even higher basicity, corresponding anhydrides may be derived. With an increase in the basicity of the acids, the complexity of the resulting anhydride is, of course, increased.

Proofs of the Constitution of Anhydrides.—In regard to the correctness of the formulas given for these anhydrides, it can only be said that they are the simplest which we can conceive of. If we acknowledge that acetic anhydride, $(C_2H_3O)_2O$, consists of two acid residues united by means of an oxygen atom, then, by analogy, it would appear that the other anhydrides, mentioned above, are constituted as represented by the formulas. But, can we assume any other formula for acetic anhydride? The acid has the constitution $C_2H_3O(OH)$; the anhydride has the empirical formula, $C_4H_6O_3$, and is formed by the simple abstraction of water from the acid; we know that the hydroxyl group has the power to separate from the acid with comparative ease. What, then, is more natural than to assume that the water which is given off from the acid is formed from the hydroxyl groups, and that the groups C_2H_3O remain undecomposed? But this would give us, besides the water, two groups, C_2H_3O and an oxygen atom. These are all combined in one molecule, and, as we believe, in such a way that the oxygen atom exerts a linking power between the two groups or acid residues, giving the formula



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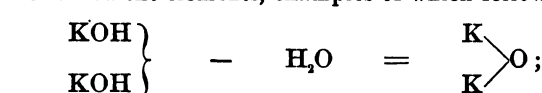
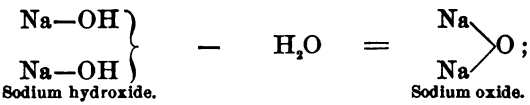
When an anhydride is formed by the abstraction of water from one molecule of an acid, the simplest conclusion we can draw is that an oxygen atom fills the place before occupied by two hydroxyl groups. We have no proof of this, to be sure, but it would be gratuitous to offer any other explanation of the formation of these anhydrides at present.

Oxides.—Just as anhydrides may be obtained from acids by the abstraction of water, so the oxides may be regarded as anhydrides of the bases. The consideration of the oxides is simpler than that of the anhydrides, because the bases themselves are generally simpler than the acids.

The simplest oxides are those obtained from the hydroxides of univalent elements, examples of which follow:

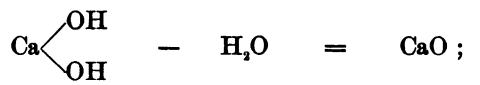


2 molecules Potassium hydroxide. Potassium oxide.

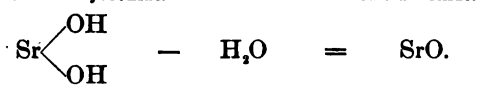


Sodium hydroxide. Sodium oxide.

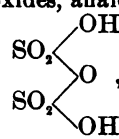
Of oxides obtained from the hydroxides of bivalent elements, we have, among others, the following;



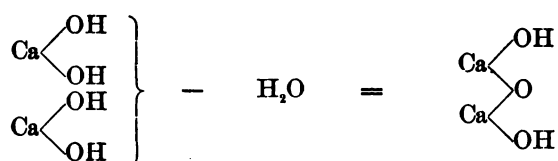
Calcium hydroxide. Calcium oxide.



Strontium hydroxide. Strontium oxide.

Theoretically, an intermediate anhydride may be formed, from either of the two preceding oxides, analogous to the formation of pyrosulphuric acid, 

, from two molecules of sulphuric acid, thus:



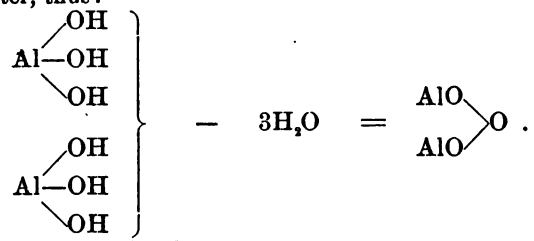
2 mol. Calcium hydroxide. Intermediate anhydride.

No such compounds have been obtained as yet.

From the hydroxides of trivalent elements we may have more than one oxide formed. If one molecule of the hydroxide loses one molecule of water, a body is formed which is oxide and hydroxide at the same time. Reference has been made to these compounds (see *ante*, p. 112), under the head of bases. The compound AlO—OH may be regarded as derived from the hydroxide $Al(OH)_3$, by the loss of one molecule of water from one molecule of the hydroxide. It is both oxide and hydroxide.

The most common method of formation of oxides from hydroxides of trivalent elements consists in the union of two

molecules of the hydroxide which then lose three molecules of water, thus:



2 mol. Aluminium hydroxide. Aluminium oxide.

The principle of the formation of these oxides is thus seen to be the same as that of the formation of anhydrides. What was said in regard to the constitution of the latter holds good in regard to the constitution of the former. The view stated is the simplest which the facts permit.

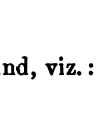
Analogy between Salts and Anhydrides and Oxides.—As we saw above, a salt is either an acid in which the hydrogen is replaced by a base residue, or a base in which the hydrogen is replaced by an acid residue. In those salts which are derived from acids containing hydroxyl, we have a base residue and an acid residue united by means of oxygen. On the other hand, in many anhydrides, we have two acid residues united by means of oxygen, while in oxides we have two base residues united by means of oxygen.

Compounds of Carbon.

We have thus briefly considered the different classes of compounds, and have seen upon what foundations our ideas in regard to the general constitution of these classes of compounds rest. Among the compounds of carbon we have many representatives of each of the classes above considered, and all that has been said holds good for these compounds; but owing to some peculiarities of carbon, which distinguish it from the other elements, certain things hold good for the carbon compounds in general, which do not hold good for

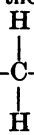
the corresponding compounds of other elements. In the following paragraphs, therefore, the *general* formulas of the different classes of carbon compounds will be briefly treated.

Hydrocarbons.—Of the compounds of carbon those which it forms with hydrogen or the hydrocarbons are, in general, the simplest, and of the hydrocarbons, marsh gas, or methane, CH_4, is the simplest one. With our present ideas in regard to constitution, there can be but one formula for this compound, viz.:



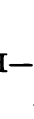
which indicates merely that a quadrivalent atom of carbon is saturated by means of four hydrogen atoms. This is the most rational supposition which we can make with reference to the compound. The formula is certainly not proved, but it is exceedingly probable. As marsh gas is a very important member of the group of carbon compounds, let us inquire more particularly concerning the grounds upon which the above formula is based. We first determine the empirical formula, CH_4, by means of analysis, and the determination of the specific gravity of the vapor of the compound. This formula is the expression of a fact and an hypothesis. The fact expressed is that methane contains 75 per cent. carbon and 25 per cent. hydrogen. The hypothesis is that the molecules of all chemical compounds, in the form of gas or vapor, have the same volume as a molecule of hydrogen. This hypothesis tells us the weights of the atoms contained in the molecule of methane and the weight of the molecule of methane, and, hence, further, the number of atoms of carbon and hydrogen contained in the molecule. Knowing the above, it remains for us to determine in what manner these atoms are united, or, what is the same thing, to determine which atoms are in combination with each other. From our knowledge of hydrogen, we assume that it acts in this compound, as in all its other compounds, as an univalent element. But if it does act thus, then two hydrogen atoms cannot be united in the molecule CH_4, for, if they were, they could not remain a part of the molecule, as their affinities would be satisfied by their action upon each other. Consequently, the hydro-

gen atoms must all be in combination with the carbon atom. This result we express by the formula



which is, further, in accordance with what we know concerning carbon, this element being usually quadrivalent.

A question which naturally suggests itself in connection with the compound CH_4 is this: Do all the hydrogen atoms play the same part in the molecule? In regard to this point, we can only say that, as far as investigations go, an affirmative answer to this question seems to be justified. If these hydrogen atoms were different, then, by replacing different ones by the same element or group, products should be obtained which are not identical. No such results have been reached, although the hydrogen atoms in methane have been replaced in a great variety of ways. It is, indeed, in these facts that the commonly accepted formula for marsh gas finds its chief support. The formula,



is the only one by which we can possibly represent each of the four hydrogen atoms as bearing the same relation to the carbon atom, if we accept the general method of representation for which the reasons were given in the introductory remarks on constitution.

Homologous Series.—Starting with methane, we have a series of hydrocarbons of the general formula C_nH_{2n+2}. These resemble each other in many respects, and differ from each other in their formulas in a very simple way. The difference in the formulas of any two contiguous members of this series is CH_2. Such a series is called an *homologous series.* A number of similar series are known. In the methane series we have: Methane, CH_4; ethane, C_2H_6; propane, C_3H_8; butane, C_4H_{10}, etc.

The general principle according to which the members of this series are formed is found in the combination of the carbon atoms in open chains. Thus, as we have seen above, if two carbon atoms combine in the sim-

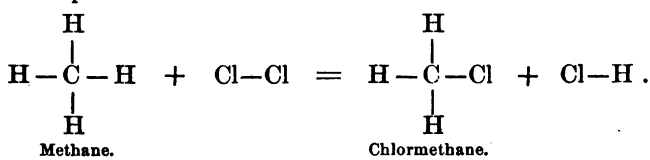
plest manner possible, viz., by one of their affinities each, a chain is formed having six free affinities, as follows:

—C—C—. If three carbon atoms combine in the same way, a chain is formed having eight free affinities, thus:

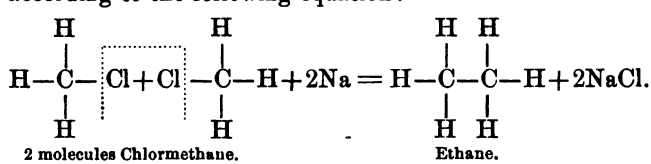
—C—C—C—. In the same way four carbon atoms combining give a chain having ten free affinities, etc., etc. By saturating these free affinities by hydrogen, we would get compounds of the formulas C_2H_6, C_3H_8, C_4H_{10}, etc., etc., which are the formulas of the hydrocarbons above given.

Experimental Proofs.—Certain experiments have been performed which appear to prove the correctness of the views in regard to the nature of the combination in the methane series of hydrocarbons.

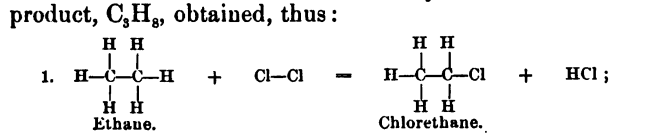
If methane is treated with chlorine, the following reaction takes place:

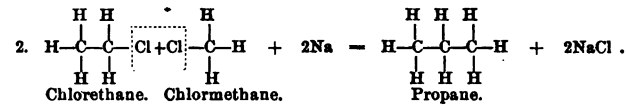


If the product is treated with sodium, the chlorine is extracted, and a compound of the formula C_2H_6 is obtained, according to the following equation:



With ethane similar reactions may be realized, and a product, C_3H_8, obtained, thus:



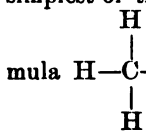


It is plain that, by continuing these reactions with the new compounds obtained, we have it in our power to build up a whole series of hydrocarbons corresponding to the series given above. If the combination always took place in the manner described, we would have simple chains, in which all the carbon atoms except those at the ends would have two free affinities, while those at the ends would have three free affinities. The hydrocarbons themselves would be respectively:

$H_3C.CH_2.CH_2.CH_3$; $H_3C.CH_2.CH_2.CH_2.CH_3$, etc., etc.

These are called *normal hydrocarbons*, to distinguish them from others of the same general composition, but of different constitution, which will be treated of in a later paragraph.

Alcohols.—Running parallel to the series of hydrocarbons which we have just considered, is a series of compounds which may be looked upon as derived from the hydrocarbons by replacing a hydrogen atom in each by the univalent group OH, or hydroxyl. These compounds are to organic chemistry what the hydroxides of the metals are to inorganic chemistry. They are known as *alcohols*. The simplest of these is derived from methane and has the formula



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Proofs.—One of the hydrogen atoms of the alcohols which contain but one oxygen atom, differs from the others. It is easily replaceable by certain groups, known as acid groups, which we shall consider hereafter. It is also replaceable by metals. In a compound of the formula CH_4O, we must assume that one hydrogen atom is in combination with the oxygen atom, while the other three are not, in order to account for its characteristic behavior. Again, if we treat the alcohol with hydrochloric acid, the oxygen atom and the peculiar hydrogen atom are given off together, and their

place is taken by a single atom of chlorine. This shows that the hydrogen and oxygen were present in the form of a univalent group, or as hydroxyl, which is the only form that satisfies these conditions.

$$\underset{\text{Methyl alcohol.}}{H_3C{-}OH} + \underset{\text{Nitric acid.}}{H(NO_3)} = \underset{\text{Methyl nitrate.}}{H_3C{-}O(NO_2)} + \underset{\text{Water.}}{H_2O.}$$

$$\underset{\text{Methyl alcohol.}}{H_3C{-}OH} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Chlormethane.}}{H_3C{-}Cl} + \underset{\text{Water.}}{H_2O.}$$

$$\underset{\text{Methyl alcohol.}}{H_3C{-}OH} + \underset{\text{Sodium.}}{Na} = \underset{\text{Sodium methyl-oxide.}}{H_3C{-}ONa} + \underset{\text{Hydrogen.}}{H.}$$

Further, the hydroxyl group can be introduced into the hydrocarbons and the alcohols thus obtained. In order to obtain the alcohol CH_4O, we may start from chlormethane, CH_3Cl. If this is treated with the hydroxide of silver, the following reaction is realized:

$$\underset{\text{Chlormethane.}}{CH_3Cl} + Ag(OH) = \underset{\text{Methyl alcohol.}}{CH_3.OH} + AgCl.$$

The above proofs suffice to show the correctness of the formula $H{-}\overset{H}{\overset{|}{C}}{-}O{-}H$ for the first member of the series of alcohols. Having once recognized the presence of hydroxyl in this alcohol, we would naturally expect to find it in the other alcohols. It is found in them all, and may be detected in the manner indicated in the case just considered.

Classes of Alcohols.—It has been found that there are three distinct classes of alcohols, which have been called, respectively, *primary*, *secondary*, and *tertiary*. These differ very markedly from each other, in their properties. This difference is particularly noticed when they are subjected to the influence of oxidizing agents, when they undergo change, as follows:

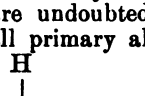
Primary alcohols are converted first into aldehydes, and then into acids containing the same number of carbon atoms.

Secondary alcohols are converted into acetones, which, when further oxidized, yield acids with a smaller number of carbon atoms.

Tertiary alcohols are decomposed without previous forma-

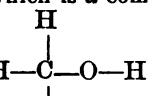
tion of aldehydes or acetones, yielding acids with a smaller number of carbon atoms.

Primary Alcohols.—These differences in the properties are undoubtedly due to differences in constitution. In all primary alcohols we find that the group $CH_2.OH$, or

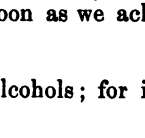


, is present. This we saw in methyl alcohol,

which is a compound of this group with hydrogen, thus:



. In ethyl alcohol, the next member of the series, this group is also present. This follows as soon as we acknowledge the presence of hydroxyl in the alcohols; for in the compound



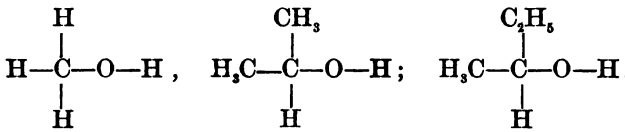
, it makes no difference which hydrogen atom is replaced by hydroxyl, the resulting compound will, in every case, have the same constitution and will necessarily contain the group $CH_2.OH$. In all alcohols which conduct themselves as primary, the presence of the group $CH_2.OH$ can be proved in a similar way. They are all derived from methyl alcohol by the replacement of a hydrogen atom with hydrocarbon residues of various composition and constitution.

By replacing a hydrogen atom with methyl, CH_3, ethyl alcohol, $CH_3.CH_2.OH$, is obtained.

By replacing a hydrogen atom with ethyl, C_2H_5, propyl alcohol, $C_2H_5.CH_2.OH$, is obtained.

By replacing a hydrogen atom with propyl, C_3H_8, butyl alcohol, $C_3H_6.CH_2.OH$, is obtained, etc.

Secondary Alcohols.—If we replace two hydrogen atoms of methyl alcohol by hydrocarbon residues, alcohols are obtained which do not contain the group $CH_2.OH$, as is evident from the following examples:

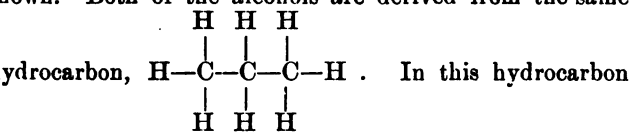


Methyl alcohol. Isopropyl alcohol. Secondary butyl alcohol.

These bodies contain the group CH.OH, and are representatives of secondary alcohols.

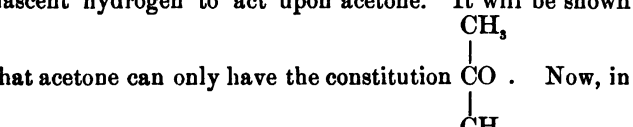
The simplest example of this class of bodies is isopropyl alcohol, the formula of which is given above.

Proofs of the General Formula of Secondary Alcohols.— There are two alcohols of the formula, C_3H_8O. One of these conducts itself like the primary alcohols, and is hence supposed to contain the group $CH_2.OH$. An alcohol isomeric with the primary alcohol cannot contain the group $CH_2.OH$, but must contain the group CH.OH, as may be readily shown. Both of the alcohols are derived from the same



In this hydrocarbon there are only two kinds of hydrogen atoms, viz., those in combination with the central carbon atom, and those in combination with the terminal carbon atoms. If we replace any one of the latter by hydroxyl, we obtain primary propyl alcohol containing the group $CH_2.OH$. Whereas, if we replace one of the former hydrogen atoms by hydroxyl, we obtain secondary propyl alcohol containing the group CH.OH. Only these two cases are possible.

But, again, this secondary alcohol is prepared by allowing nascent hydrogen to act upon acetone. It will be shown



Now, in its conversion into secondary propyl alcohol, acetone takes up two atoms of hydrogen, and the only place where these hydrogen atoms can find entrance into the above molecule is at the central carbon atom. One of the bonds of union between the oxygen and carbon is loosened, and hydroxyl is

formed; thus the carbon atom becomes possessed of a free affinity, which is at once saturated with hydrogen, and we have the group CH.OH or $H-\overset{|}{\underset{|}{C}}-O-H$, which is bivalent.

The proof, as will be observed, is to some extent, dependent on the valence hypothesis. Accepting the formula for acetone, $\begin{matrix} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{matrix}$, for which the proof will be given, the conversion into isopropyl alcohol furnishes evidence that the hydroxyl in the alcohol is probably united with the central carbon.

Similar considerations, in connection with other secondary alcohols, lead to similar results, and hence the conclusion is drawn that all secondary alcohols contain the group CH.OH.

Tertiary Alcohols.—If we replace three hydrogen atoms of methyl alcohol by hydrocarbon residues, alcohols are obtained which contain neither the group $CH_2.OH$, nor the group CH.OH, as may be seen in the following examples:

$\begin{matrix} H \\ | \\ H-C-O-H \\ | \\ H \end{matrix}$, $\begin{matrix} CH_3 \\ | \\ CH_3-C-O-H \\ | \\ CH_3 \end{matrix}$, $\begin{matrix} C_2H_5 \\ | \\ CH_3-C-O-H \\ | \\ CH_3 \end{matrix}$.

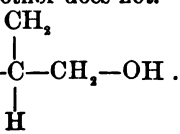
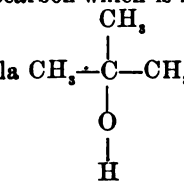
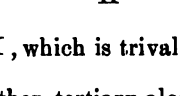
Methyl alcohol. Tertiary butyl alcohol. Tertiary amyl alcohol.

These bodies contain the group C.OH, and are representatives of tertiary alcohols.

The simplest example of this class of alcohols is tertiary butyl alcohol, $C_4H_{10}O$, the constitution of which is indicated by the formula given above.

Proofs.—The proofs for the correctness of this formula are the following:

There is a hydrocarbon, the formula of which can be shown to be $\begin{matrix} CH_3 \\ | \\ CH_3-C-CH_3 \\ | \\ H \end{matrix}$. From this two alcohols are

derived, one of which conducts itself as a primary alcohol, while the other does not. The former must have the formula  . The only alcohol derived from this hydrocarbon which is not a primary alcohol must have the formula  , and hence contains the group  , which is trivalent. Further, similar considerations of other tertiary alcohols indicate that in them also the group C.OH is contained, and, consequently, this is looked upon as the characteristic group of these bodies.

Determination of Alcohols.—With the knowledge thus gained with reference to alcohols in general, it is plain that we have it in our power to determine in any particular case, 1, whether the body we are dealing with is an alcohol, and, 2, whether it is a primary, secondary, or tertiary alcohol. The first thing to be done is to determine whether the body contains hydroxyl or not. Treatment with the chlorides of phosphorus, either the trichloride or pentachloride, is one of the best means of making this determination. If, by treatment with the chloride, a product is obtained, containing one atom of chlorine in the molecule in the place of an oxygen atom and a hydrogen atom, we can assume that hydroxyl was present. If this hydroxyl is the alcoholic hydroxyl, then its hydrogen must be capable of replacement by the so-called acid groups. To determine this, acetyl chloride, $C_2H_3O.Cl$, is very frequently employed. If this body is allowed to act upon a substance containing an alcoholic hydroxyl group, the chlorine of the chloride combines with the hydrogen of the hydroxyl, forming hydrochloric acid, and the acid group C_2H_3O takes the place of the hydrogen, thus:

$$\underset{\text{Alcohol.}}{R{-}OH^{*}} + \underset{\text{Acetyl chloride.}}{C_2H_3O.Cl} = \underset{\text{New product.}}{R{-}O{-}C_2H_3O} + HCl.$$

If the reaction takes place in this manner, we are justified in concluding that the hydroxyl group is alcoholic, or that the body under examination is an alcohol.

It remains still to determine whether the alcohol is primary, secondary, or tertiary. This can be accomplished by subjecting it to the influence of oxidizing agents.

If it yields an aldehyde, and then an acid containing the same number of carbon atoms, it is a primary alcohol.

If it yields first an acetone, and then by further oxidation breaks up, yielding an acid or acids containing a smaller number of carbon atoms, it is a secondary alcohol.

If, without first yielding an aldehyde or an acetone, it breaks up directly with the formation of an acid containing a smaller number of carbon atoms, it is a tertiary alcohol.

The above tests, then, enable us to determine a part of the constitutional formulas of many compounds. If we have, by means of these tests, determined that a compound is a primary alcohol, we assume that it contains the group $CH_2.OH$. If it is a secondary alcohol, it contains the group CH.OH. And, if it is a tertiary alcohol, it contains the group C.OH. But these groups may enter into a great variety of compounds, and, frequently, after we have determined the presence of one or the other of these groups, it would still be necessary to determine the constitution of the group with which it is combined. These special determinations will be considered later.

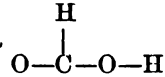
Mercaptans.—If, in place of hydroxyl, in the alcohols we have considered, we introduce the group HS, bodies are obtained, which have been called mercaptans. These are, in many respects, analogous to alcohols, though in their reactions they differ from them somewhat. Their constitution is similar to that of the alcohols. The principal method for their formation consists in the action of potassium sulphydrate, KSH, on the chlorides of alcohol residues. These latter are obtained by replacing the hydroxyl of alcohols by chlorine, and the reaction for the formation of the mercaptans takes place as follows:

* In this formula, and in others which will follow, R stands for any hydrocarbon residue which is univalent, as CH_3, C_2H_5, etc.

$$\underset{\text{Alcoholic chloride.}}{RCl} + K—SH = \underset{\text{Mercaptan.}}{R—SH} + KCl.$$

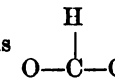
It will thus be seen that the group SH occupies the place, which was occupied by the group OH in the original alcohol. Theoretically, a mercaptan may be prepared corresponding to every alcohol. Thus we might have primary, secondary, and tertiary mercaptans, corresponding to all the known primary, secondary, and tertiary alcohols. Only such mercaptans have been prepared up to the present as correspond to the primary alcohols.

Acids.—What has been said above concerning acids in general is true of the acids of carbon. They contain hydroxyl, and possess the properties which we have recognized as belonging to acids. In general, they are weaker than other acids, though they differ among each other in strength between comparatively wide limits. We have several series of acids of carbon, corresponding to the series of hydrocarbons and alcohols. The simplest carbon acid is derived from methane, and has the formula



It differs from the simplest alcohol in containing an atom of oxygen in the place of two atoms of hydrogen. Just as this alcohol consists of hydrogen combined with the group $CH_2.OH$, so the acid consists of hydrogen combined with the group CO.OH. This is the characteristic group of the acids of carbon.

Proofs.—In the first place, the presence of hydroxyl is proved the same as in the case of ordinary acids. In the acid H_2CO_2, if we assume the presence of hydroxyl, we have the formula HCO—OH. Further, the other hydrogen atom contained in the acid does not conduct itself as if it were in combination with oxygen, but rather like hydrogen atoms, which are in combination with carbon directly. No changes which the acid undergoes, indicate any connection between this hydrogen atom and oxygen atom, so we may conclude that they are not present as hydroxyl. But, if they are not present as hydroxyl, they must be united directly with the carbon atom, and the

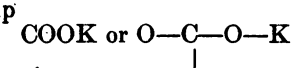
formula is  . Now, by certain reactions, it is possible to replace that hydrogen atom in the acid, which is in direct combination with the carbon by groups such as CH_3, C_2H_5, etc. The compounds thus obtained must contain the group CO.OH. They possess all the properties of acids.

Methods for the Formation of the Acids of Carbon.—The methods of preparation of the acids of carbon enable us also to judge of their constitution. Some of these methods may be briefly described.

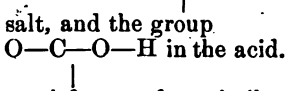
1. The simplest acid, above referred to, viz., H_2CO_2, is obtained by bringing carbon monoxide, CO, together with potassium hydroxide, KOH. The two substances combine directly, yielding the potassium salt of the above acid, thus:

$$CO + KOH = HCO_2K.$$

From this experiment we conclude that, in the salt, one of the oxygen atoms is in direct combination with carbon, as it was in carbon monoxide, while the other oxygen atom serves the purpose of linking the carbon atom to potassium. Hence the group



is present in the salt, and the group



in the acid.

This proof is unsatisfactory, for a similar argument might be used to show that the hydrogen in the salt, HCO_2K, is in direct combination with oxygen.

2. When certain hydrocarbons are allowed to act upon carbonyl chloride, $COCl_2$, one of the chlorine atoms is replaced by a residue, as may be illustrated thus:

$$\text{(I.)}\quad CH_4 + COCl_2 = CH_3.COCl + HCl.$$

When the product is treated with water, the second chlorine atom is replaced by OH, as follows:

$$\text{(II.)}\quad CH_3.COCl + HHO = CH_3.CO.OH + HCl.$$

Now carbonyl chloride is obtained by the direct addition of chlorine, Cl_2, to carbon monoxide, CO; and hence must have the constitution $CO\begin{matrix}Cl\\Cl\end{matrix}$. The simplest interpretation of reaction (I.) above is that the residue CH_3 takes the place occupied by one of the chlorine atoms, which would give $CO\begin{matrix}CH_3\\Cl\end{matrix}$. Lastly, the simplest interpretation of reaction (II.) is that the hydroxyl group enters into the place of the second chlorine atom, which gives as the constitution of the product $CO\begin{matrix}CH_3\\OH\end{matrix}$. This product is acetic acid, a homologue of the simplest acid of carbon. It contains the group CO.OH.

3. The compound cyanogen, $\begin{matrix}CN\\|\\CN\end{matrix}$, is converted into an acid by the action of water. This acid has the formula $C_2H_2O_4$. It is a bibasic acid and hence contains two hydroxyl groups, which would lead to the formula $C_2O_2(OH)_2$. As both the hydroxyl groups conduct themselves in exactly the same way, it is concluded that they are combined in exactly the same way. The only formula that satisfies these conditions is $\begin{matrix}OH\\|\\CO\\|\\CO\\|\\OH\end{matrix}$. In this compound we have two groups CO.OH, and, as we have seen, it is a bibasic acid. There are a great many compounds, containing the group CN, acting as a univalent group. By treating these with solutions of metallic hydroxides, the nitrogen is given off in the form of ammonia, NH_3, and in its place are taken up two atoms of oxygen and one atom of a univalent element. The group, with which the CN is in combination, remains unchanged. Hence, in accordance with the above experiment, it is believed that this reaction consists in a conversion of the group CN into COOH or COOM,

in which M represents one atom of a univalent metal. The constitution of this group is, of course, expressed as above by the formula $\begin{matrix} O—C—O—H \\ | \end{matrix}$. All the substances thus prepared, and containing this group, are derivatives of the acids; they are salts.

4. Using the valence hypothesis as a basis, the following arguments may be employed: The acids are derived from primary alcohols by simple oxidation. When an acid is obtained from either a secondary or a tertiary alcohol, a complex oxidation takes place; the molecule must be broken up and rearranged. We have seen that the difference between the three classes of alcohols is due to the difference in the characteristic groups of each class; these being CH_2OH, CHOH, and COH. The oxidation consists in the abstraction of hydrogen and addition of oxygen. If hydrogen is abstracted from, and oxygen added to, the group CH_2OH, we obtain COOH or $\begin{matrix} O—C—O—H \\ | \end{matrix}$. If we abstract hydrogen from, and add oxygen to, the group CHOH, which is bivalent, we could not obtain another bivalent group, unless it be one with an exceedingly improbable formula, as, for instance, $—C\begin{matrix} O \\ | \\ O \end{matrix}$, and this would contain no hydrogen, so that it could not be considered as characteristic of acids. Lastly, the group COH cannot lose hydrogen and gain oxygen, and still remain trivalent. As, then, the only alcohols, which can yield the group COOH by the oxidation of their own characteristic group, are the primary alcohols, and as those alcohols, which cannot yield this group by such oxidation, do not yield corresponding acids, the conclusion is drawn that the change, which takes place when primary alcohols are oxidized, consists in the conversion of the group $\begin{matrix} H \\ | \\ —C—O—H \\ | \\ H \end{matrix}$ into $\begin{matrix} \\ | \\ O—C—O—H \end{matrix}$, which is a necessary constituent of carbon acids.

Aldehydes.—Aldehydes are products derived from the partial oxidation of primary alcohols, the group CH_2OH

being converted into COH. This group is not identical with the group —C(|)—O—H of tertiary alcohols, but has the constitution expressed by the formula O—C(|)—H. It is univalent, just as the group CH_2OH, from which it is derived, is univalent; whereas, the tertiary alcohol group, COH, is trivalent. The aldehydes are intermediate products between primary alcohols and the acids which these yield. It was shown that the acids are formed from these alcohols by the extraction of hydrogen and addition of oxygen. If hydrogen is only abstracted, and no oxygen added, the product is an aldehyde, thus:

$R—CH_2OH$,	$R—COH$,	$R—COOH$.
Primary alcohol.	Aldehyde.	Acid.

Proofs.—The proofs of the general constitution of aldehydes are similar to those given for the acids. Take, for instance, the simplest aldehyde. This has the formula H_2CO. The tests for the presence of hydroxyl, above considered, if applied to aldehydes, show that the group is not present. On the contrary, if the aldehydes be treated with the chlorides of phosphorus, the oxygen atom is extracted and its place is taken by *two* chlorine atoms. This shows that the oxygen was held in combination by the carbon atom in quite a different way from that which is characteristic of hydroxyl, and, consequently, it could not have been present in combination with hydrogen, forming hydroxyl. We are thus led to the formula O—C(H)—H for the above compound. It consists of a hydrogen atom combined with the group —C(H)—O. Other aldehydes are derived from this simplest one by replacing one of the hydrogen atoms by a residue of greater or less complexity. Thus, we may introduce the group CH_3 or C_2H_5, and we obtain the compounds $CH_3—COH$, and $C_2H_5—COH$, respectively, both of which are aldehydes.

The methods for the preparation of aldehydes also fur-

nish proof of the constitution above ascribed to them. Some of these are the following:

1. We have already seen that, when an acid is treated with the chloride of phosphorus, its hydroxyl is replaced by an atom of chlorine. Each such chloride, as was shown, contains the group $-\overset{\overset{Cl}{|}}{C}-O$. If we could replace the chlorine atom in this group by hydrogen, we would plainly have the characteristic aldehyde group $-\overset{\overset{H}{|}}{C}-O$. Such a replacement has been effected in the case of some of the chlorides, and the resulting bodies were found to be the expected aldehydes.

2. When a salt of any acid of carbon is mixed with a salt of the simplest acid of carbon (formic acid), of the formula H.CO.OH, and the mixture distilled, an aldehyde is formed, together with a carbonate. The carbonates are derived from a bibasic acid, and have the formula $CO\langle^{OM}_{OM}$. It seems rational to suppose that the groups OM have passed directly from the compounds in which they were originally contained to the carbonate, and that the group CO has also been derived directly from one of the original acids. If these suppositions are correct, then we are led to the conclusion that the aldehyde resulting from the described reaction contains the group $\overset{\overset{H}{|}}{C}-O$. For, let R—CO.OM represent the formula of any salt of a carbon acid, and H.CO.OM a salt of formic acid. On bringing these two compounds together and heating them, either one of two things can take place if the above suppositions are correct. The groups forming the carbonate may be split off thus:

$$\left.\begin{array}{l} R-\boxed{CO-OM} \\ H-CO-\boxed{OM} \end{array}\right. ;$$

or, thus:

$$\left.\begin{array}{l} R-CO-\boxed{OM} \\ H-\boxed{CO-OM} \end{array}\right. .$$

The remaining groups, uniting in the simplest way, will give us, in either case, a compound, $R-\overset{H}{\overset{|}{C}}-O$.

3. Aldehydes are formed only from primary alcohols, not from secondary or tertiary alcohols. If we examine the formula of the groups characteristic of the alcohols, we shall find that the only one which is capable of transformation into the group $\overset{H}{\overset{|}{C}}-O$ is that of primary alcohols, $-CH_2OH$; and, further, the group $\overset{H}{\overset{|}{C}}-O$ is the only one containing carbon, hydrogen, and oxygen in the same proportions, which can be derived from the group of primary alcohols, and not from those of secondary and tertiary alcohols.

These considerations make it exceedingly probable that all aldehydes contain the group $\overset{H}{\overset{|}{C}}-O$, as above stated.

Acetones.—Acetones are products of the partial oxidation of secondary alcohols, the group $-\overset{|}{\underset{H}{\overset{|}{C}}}-OH$ being converted into $\overset{|}{\underset{|}{CO}}$. The aldehydes, too, contain the group $\overset{|}{\underset{|}{CO}}$; but it is further characteristic of aldehydes that one of the affinities of this group is saturated with hydrogen, giving the complete group $\overset{CO}{\underset{H}{|}}$. On the other hand, it is characteristic of acetones that both of the affinities of the group $\overset{|}{\underset{|}{CO}}$ are saturated with hydrocarbon residues.

Thus the simplest acetone known has the formula $CH_3-CO-CH_3$, both of the affinities of the characteristic group being saturated with residues of the hydrocarbon methane, CH_4.

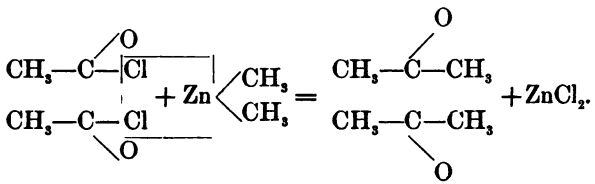
Proofs.—As just stated, the simplest acetone has the formula C_3H_6O. If a chloride of phosphorus be allowed to act upon this compound, the result is similar to that obtained in the same experiment with aldehydes, viz., the atom of oxygen is abstracted, and two chlorine atoms take its place. This shows that the oxygen was not present as hydroxyl, but was combined with the carbon atom by means of two affinities, forming the group $-CO-$.

Again, if nascent hydrogen is allowed to act upon this acetone, secondary propyl alcohol is the product, and the alcohol has the formula $CH_3-CH(OH)-CH_3$. From this we conclude that in acetone, as well as in secondary propyl alcohol, the two groups CH_3 are present; and we are thus led to the formula $CH_3-CO-CH_3$ for the simplest acetone. We recognize in this formula what we have stated to be the characteristic of all acetones, viz., it consists of two hydrocarbon residues combined by means of the bivalent group $-CO-$.

The following methods of preparation serve as proofs of the accepted constitution of acetones:

1. Just as aldehydes are obtained from acid chlorides by replacing the chlorine by hydrogen, so acetones are

obtained from the same chlorides by replacing the chlorine by hydrocarbon residues. By treating acetyl chloride, $C_2H_3O.Cl$, with zinc methyl, $Zn(CH_3)_2$, ordinary acetone, $CO(CH_3)_2$, is produced, together with zinc chloride, $ZnCl_2$. The formula of acetyl chloride is known to be $CH_3—C(Cl)—O$. Hence the simplest interpretation of the above reaction is that a methyl group of zinc methyl takes the place of a chlorine atom in acetyl chloride, thus:



And this leads us clearly to the formula above assumed as representing the constitution of acetone.

2. When the salts of many acids of carbon are subjected to dry distillation, acetones are formed, together with a carbonate or carbonates. This reaction is analogous to the reaction for the preparation of aldehydes, by the distillation of a mixture of the salt of some carbon acid and a salt of formic acid. What was said in regard to the latter reaction, showing that the group $C(=O)—$ must be present in aldehydes, holds good in regard to the reaction under consideration, and shows just as conclusively that the group $C(=O)—$ must be present in acetones. Let R.CO.OM represent a salt of an acid of carbon. Its decomposition by heat may be represented as follows:

$$\begin{matrix} R. & CO.OM \\ R.CO. & OM \end{matrix}$$

The residues uniting, we have a compound, R—CO—R, which has the general formula of an acetone, as above assumed. Or let R.COOM represent the salt of one carbon acid and R'.COOM the salt of another carbon acid, in

which R and R′ are both hydrocarbon residues. The decomposition, which takes place when a mixture of these two salts is heated, is represented as follows:

$$\begin{matrix} R.COOM \\ R'.COOM \end{matrix}$$

This gives a compound of the formula R—CO—R′.

It will be seen that one of the first conditions for the production of an acetone by means of this reaction is that neither of the salts employed be a formate, H.COOM, as the use of the latter would give rise to the formation of an aldehyde.

3. Acetones are produced by the partial oxidation of secondary alcohols. Considerations, similar to those employed in the cases of acids and aldehydes, show that the supposition that the group $\begin{matrix} | \\ CO \\ | \end{matrix}$ is present in acetones, is most in harmony with the fact of the ready transformation of secondary alcohols into acetones.

Ethers.—In general when acids and bases act upon each other salts are formed, water being eliminated. So, also, when alcohols and carbon acids act upon each other, bodies similar to salts are formed, water being eliminated:

$$\underset{\text{Formic acid.}}{H.COOH} + \underset{\text{Alcohol.}}{C_2H_5.OH} = \underset{\text{New body.}}{H.CO.OC_2H_5} + H_2O;$$

$$\underset{\text{Sulphuric acid.}}{SO_2\begin{matrix}OH \\ OH\end{matrix}} + \underset{\text{Methyl alcohol.}}{2CH_3.OH} = \underset{\text{New body.}}{SO_2\begin{matrix}O.CH_3 \\ O.CH_3\end{matrix}} + 2H_2O\,.$$

$$\underset{\text{Nitric acid.}}{NO_2—OH} + \underset{\text{Alcohol.}}{C_2H_5—OH} = \underset{\text{New body.}}{NO_2—OC_2H_5} + H_2O.$$

It will be seen that these bodies differ from salts in that they contain hydrocarbon residues in the place of metals. Salts were defined as acids in which the hydrogen of the hydroxyl group is replaced by a base residue. These bodies are acids in which the hydrogen of the hydroxyl group is replaced by a hydrocarbon residue. All bodies of this kind are called ethers, and to distinguish them from another class of bodies known as *simple ethers*, and which will be con-

sidered below, they are usually known as *compound ethers*. The analogy between compound ethers and salts is very close, and hence, if the nature of salts is understood, the nature of these ethers will also be readily understood. We may have compound ethers derived from monobasic, bibasic, tribasic, etc., acids, and we may have compound ethers containing univalent, bivalent, trivalent, etc., hydrocarbon residues; as for instance,

Ethers of monobasic acids:

$NO_2.O.C_2H_5$, $CH_3.CO.O.CH_3$, etc.
Ethyl nitrate. Methyl acetate.

Ethers of bibasic acids:

$SO_2\langle^{O.CH_3}_{O.CH_3}$, $C_2H_4\langle^{CO.O.C_2H_5}_{CO.O.C_2H_5}$, etc.
Methyl sulphate. Ethyl succinate.

Ethers of tribasic acids:

$PO\langle^{O.C_2H_5}_{O.C_2H_5}_{O.C_2H_5}$, $C_3H_5\langle^{CO.O.C_2H_5}_{CO.O.C_2H_5}_{CO.O.C_2H_5}$, etc.
Ethyl phosphate. Ethyl tricarballyate.

The above ethers all contain univalent hydrocarbon residues. Among those containing bivalent residues may be mentioned:

$CH_3.CO.O\rangle C_2H_4$.
$CH_3.CO.O\rangle$
Ethylene diacetate.

Proofs.—The fact that compound ethers are, in many cases, formed by the direct action of acids upon alcohols, and that water is formed at the same time, taken together with our knowledge concerning the constitution of acids and alcohols, points clearly to the constitution which has been above assumed for these ethers. But another method of formation is just as decisive in its testimony.

If the silver salts of acids are treated with the chlorides, bromides, or iodides of hydrocarbon residues, compound ethers are formed in which the hydrocarbon residues are found in the place of the silver which was in the salts, and

the silver itself is found in combination with the chlorine, bromine, or iodine which was in combination with the hydrocarbon residues. This is seen in the following typical reactions:

$$\underset{\text{Silver acetate.}}{CH_3.CO.OAg} + \underset{\text{Ethyl iodide.}}{C_2H_5I} = \underset{\text{Ethyl acetate.}}{CH_3.CO.O.C_2H_5} + AgI.$$

$$\underset{\text{Silver succinate.}}{C_2H_4\begin{matrix}CO.OAg\\CO.OAg\end{matrix}} + \underset{\text{Methyl iodide.}}{2(CH_3I)} = \underset{\text{Methyl succinate.}}{C_2H_4\begin{matrix}CO.OCH_3\\CO.OCH_3\end{matrix}} + 2AgI.$$

Simple Ethers.—Simple ethers correspond to the metallic oxides. They consist of two hydrocarbon residues, united by means of an oxygen atom, just as the metallic oxides consist of two base residues united by means of an oxygen atom. Examples of these are the following:

$$\underset{\text{Methyl ether.}}{CH_3\diagdown O\diagup CH_3}, \quad \underset{\text{Methyl-ethyl ether.}}{C_2H_5\diagdown O\diagup CH_3}, \quad \underset{\text{Ethyl ether.}}{C_2H_5\diagdown O\diagup C_2H_5}, \quad \text{etc.}$$

Proofs.—The constitution of these compounds is rendered clear by a consideration of one of the principal methods of their formation.

When an alcohol is treated with sodium or potassium, as we have seen, the hydrogen of the hydroxyl is replaced by the metal employed. We thus obtain compounds, such as sodium ethyloxide $C_2H_5.ONa$, sodium methyloxide $CH_3.ONa$, etc. If these compounds are further treated with the iodides of hydrocarbon residues, the iodine combines with the metal and the residues unite. Thus we have the following reactions:

$$\underset{\text{Sodium ethylate.}}{C_2H_5.ONa} + \underset{\text{Ethyl iodide.}}{C_2H_5I} = \underset{\text{Ethyl ether.}}{C_2H_5—O—C_2H_5} + NaI,$$

$$\underset{\text{Sodium methylate.}}{CH_3.ONa} + \underset{\text{Methyl iodide.}}{CH_3I} = \underset{\text{Methyl ether.}}{CH_3—O—CH_3} + NaI,$$

$$\underset{\text{Sodium methylate.}}{CH_3.ONa} + \underset{\text{Ethyl iodide.}}{C_2H_5I} = \underset{\text{Methyl-ethyl ether.}}{CH_3—O—C_2H_5} + NaI,$$

$$\underset{\text{Sodium ethylate.}}{C_2H_5.ONa} + \underset{\text{Methyl iodide.}}{CH_3I} = \underset{\text{Methyl-ethyl ether.}}{C_2H_5—O—CH_3} + NaI.$$

From these reactions we see what the constitution of the ethers formed must be. We are in each case justified in

assuming that the hydrocarbon residue enters into the new compound in the place occupied by the metal, and, according to our conceptions concerning alcohols, this metal is united to the rest of the molecule in which it is contained by means of an oxygen atom.

Anhydrides.—The anhydrides of carbon compounds are derived from carbon acids in the same way that anhydrides in general are derived from acids; and all the possibilities which we considered above hold good for these anhydrides. There are anhydrides derived from monobasic, bibasic, tribasic acids, etc. There are partial and complete anhydrides; but, further, there are anhydrides derived from compounds which partake of the double character of alcohol and acid. In these compounds the hydroxyl which imparts the alcoholic character and that which imparts the acid character, both together furnish the elements which form the water given off.

Substitution Products.

We have thus far considered the various classes of chemical compounds which are known to exist, and it has been shown that each class is characterized by some peculiarity of constitution which is recognized in each member of the class. There is in each compound a group which determines its character, making it an acid or an alcohol, an acetone or an aldehyde, etc. As long as this group remains unchanged, the compound belongs to the same class. If the group is changed, the compound loses its characteristics, and belongs to another class. On the other hand, the hydrocarbon residues with which the class groups are united may undergo a variety of changes without interfering with the general properties of the compounds. The most common of these changes are those which are effected by substitution.

Chemical compounds act upon each other, in general, in two ways: 1st. They unite directly, forming only one product, as in the following reactions:

$$\underset{\text{Ammonia.}}{NH_3} + HCl = \underset{\text{Ammonium chloride.}}{NH_4Cl}$$

$$\underset{\text{Ethylene.}}{C_2H_4} + Br_2 = \underset{\text{Ethylene bromide.}}{C_2H_4Br_2}$$

2d. They exchange certain constituents, forming two or more new products, thus:

$$\underset{\text{Ethane.}}{C_2H_6} + Cl_2 = \underset{\text{Chlorethane.}}{C_2H_5Cl} + HCl$$

$$\underset{\text{Aldehyde.}}{CH_3.COH} + 6Cl = \underset{\text{Trichloraldehyde.}}{CCl_3.COH} + 3HCl$$

$$\underset{\text{Benzene.}}{C_6H_6} + H_2SO_4 = \underset{\text{Benzenesulphonic acid.}}{C_6H_5.SO_3H} + H_2O$$

$$\underset{\text{Benzene.}}{C_6H_6} + HNO_3 = \underset{\text{Nitrobenzene.}}{C_6H_5(NO_2)} + H_2O\ .$$

The latter kind of action is by far the most common. It is that which is called substitution. In the above examples, the principal products are called substitution products, though, strictly speaking, both products are substitution products.

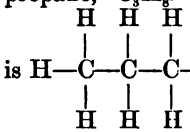
While the principle of substitution is recognized in connection with nearly all chemical reactions, and hence nearly all chemical compounds may be considered as substitution products, with reference to some other compounds, still it is customary to include under this head only those which are formed by the replacement of hydrogen in carbon compounds, and the substitutions, which are spoken of, are only those which can be actually effected—not imaginary cases.

Substitution Products containing Chlorine, Bromine, or Iodine.—The simplest examples of substitution products are those which are formed by the action of any of the so-called halogens (Cl, Br, I) upon carbon compounds. The action consists in the abstraction of one or more atoms of hydrogen from the compound, and the filling of the places left vacant by a corresponding number of atoms of the substituting element. The constitution of the products is the same as that of the compounds from which they are derived. Thus we have acetic acid, $CH_3.CO.OH$; if chlorine acts upon it, the following reactions take place successively:

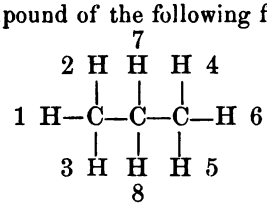
$$CH_3.CO.OH + Cl_2 = CH_2Cl.CO.OH + HCl.$$
$$CH_2Cl.CO.OH + Cl_2 = CHCl_2.CO.OH + HCl.$$
$$CHCl_2.CO.OH + Cl_2 = CCl_3.CO.OH + HCl.$$

The constitution of these three different products is essentially the same as that of the acid from which they are derived.

Among these simple substitution products, however, differences are possible, and are actually observed, which are not possible in the original compounds. Take the compound propane, C_3H_8. The constitution of this hydrocarbon is



. The hydrogen atoms cannot be arranged in any other way with reference to the carbon atoms. On the basis of the formula there is only one hydrocarbon of this composition possible. But the carbon atoms in the compound differ from each other. The two, which are represented as ending the chain in the formula, are alike, while the central atom differs from them. The first are in combination with carbon by means of only one affinity each, while the central atom is joined to carbon by means of two affinities. We would naturally expect, then, that the difference between these two kinds of carbon atoms would cause a difference between the hydrogen atoms combined with them. If such a difference exists, then, different products must be obtained according as we replace a hydrogen atom attached to one of the terminal carbon atoms, or another hydrogen atom attached to the central carbon atom. Thus if in a compound of the following formula,



we replace any one of the hydrogen atoms, numbered 1, 2, 3, 4, 5, 6, by an element, such as chlorine, the resulting compound should in each case be the same.

If, however, we replace one of the hydrogen atoms, numbered 7 or 8, by the same element, a compound of the same composition, but of different constitution, should be obtained. The formulas of the two compounds would be respectively

$CH_2Cl.CH_2.CH_3$ and $CH_3.CHCl.CH_3$.

Thus, we see that the position of a substituting element must be taken into consideration in studying the constitution of compounds. In connection with the individual compounds, which will be briefly considered in the last section of this book, the methods will be described which enable us to determine the positions of substituting elements and groups.

Complex Substitution Products.—Under this head we include all those products which are formed by replacing the hydrogen of a carbon compound either partially or wholly by groups. In accordance with what has just been said concerning the simple substitution products, it is plain that, in studying the constitution of the complex substitution products, two things must be taken into consideration:

1st. The constitution of the substituting group itself, and,

2d. The position of the group in the molecule of the substitution product.

Only the first part of the problem will be taken up here.

Constitution of Substituting Groups.—The groups which we shall have to consider are the following: The cyanogen group CN, and an isomeric group; the sulpho group SO_3H; the nitro group NO_2; the nitroso group NO; the amido group NH_2; the imido group NH; and a few other groups intimately connected with those mentioned.

Constitution of the Group CN.—That acid of carbon, which consists of a nitrogen atom and a hydrogen atom, united with a carbon atom, viz., hydrocyanic acid, has already been referred to. By appropriate reactions it is possible to transfer the group CN, contained in hydrocyanic acid, to other compounds in such a way that it takes the place of hydrogen, forming a substitution product. It is expressed by the formula —C—N . We have the following reactions:

$$\underset{\text{Monochloracetic acid.}}{CH_2Cl.COOH} + \underset{\text{Potassium cyanide.}}{KCN} = \underset{\text{Cyanacetic acid.}}{CH_2(CN).COOH} + KCl;$$

$$\underset{\text{Ethylene bromide.}}{C_2H_4Br_2} + \underset{\text{Potassium cyanide.}}{2KCN} = \underset{\text{Ethylene cyanide.}}{C_2H_4(CN)_2} + 2KCl.$$

Those substitution products which consist only of the group —C—N combined with a hydrocarbon residue, are called *cyanides* or *nitriles*.

A few other compounds are known, which have the same composition as the nitriles, but a different constitution. They are known as *isonitriles* or *carbamines*. The difference between the cyanides and carbamines is supposed to consist in the fact that in the former the carbon of the group CN is the linking atom, while in the latter the nitrogen performs this function. This difference is expressed, in the case of the ethyl compounds, by the formulas $C_2H_5—C—N$ for the cyanide, and $C_2H_5—N—C$ for the carbamine. These formulas are based upon the reactions of the two classes of compounds. The reactions are as follows:

Ethyl cyanide, $C_2H_5.CN$, when treated with an alkali, yields propionic acid $C_2H_5.CO.OH$. The nitrogen is given off, and oxygen and hydrogen take its place. The carbon remains united to the residue C_2H_5. We hence conclude that in the cyanide the carbon atom of the group CN is united directly with the hydrocarbon residue. For, if it had not been, the removal of the nitrogen ought to have caused the formation of a product containing a smaller number of carbon atoms than the cyanide itself. The reaction which does actually take place, is that which we have considered above, as giving rise to the formation of acids from the cyanides, viz.:

$$\underset{\text{Ethyl cyanide.}}{C_2H_5.CN} + 2H_2O = \underset{\text{Propionic acid.}}{C_2H_5.COOH} + NH_3.$$

If the group CN had been in combination with the hydrocarbon residue by means of the nitrogen atom, we should expect the nitrogen atom to remain in combination with the hydrocarbon residue, in case of decomposition, or we should expect the nitrogen atom to take with it the carbon atom, with which it is most intimately combined. In either case, a separation of the carbon atoms would be the result, and we would obtain products containing a smaller number of carbon atoms than the original compound contained. This is exactly what takes place when the carbamines are decomposed. When treated with hydrochloric acid, they yield two products; one of these is formic acid, a compound containing one atom of carbon; the other consists of the hydrocarbon residue of the original compound combined with

the nitrogen atom and hydrogen. Thus, in the case of ethylcarbamine, the decomposition may be represented as follows:

$$\underset{\text{Ethylcarbamine.}}{C_2H_5{-}N{=}C} + 2H_2O = \underset{\text{Ethylamine.}}{\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N} + \underset{\text{Formic acid.}}{H.COOH}$$

The fact that the compound $N\left\{\begin{matrix}C_2H_5\\H\\H\end{matrix}\right.$, in which the nitrogen atom is evidently in combination with the hydrocarbon residue, is so readily formed, leads to the conclusion that, in the original compound, the same kind of union existed. The fact, also, that the one carbon atom is given off so readily from the molecule, indicates clearly that it was held in combination in some manner different from that in which the other carbon atoms of the molecule are held in combination.

In the terms of the valence hypothesis, the difference between the cyanides and carbamines is explained by assuming that, in the former, the CN group has the constitution —C≡N, while, in the latter, it is C≡N—. In the one case the nitrogen is supposed to act as a triad, in the other as a pentad.

Constitution of the Group SO_3H.—By the action of concentrated sulphuric acid upon hydrocarbons and various other compounds containing hydrogen, derivatives are obtained, which differ from the original compounds in containing the group SO_3H in the place of hydrogen. The reaction consists in the formation of water and the new derivative, thus:

$$\underset{\text{Benzene.}}{C_6H_6} + SO_2\!\!<\!\!\begin{matrix}OH\\OH\end{matrix} = \underset{\text{Benzenesulphonic acid.}}{SO_2\!\!<\!\!\begin{matrix}C_6H_5\\OH\end{matrix}} + H_2O.$$

These products all act like acids in every way, so that we are justified in assuming the presence of hydroxyl in them. As they are formed so readily from sulphuric acid, it is also fair to assume that the group SO_2OH is a residue of sulphuric acid. Then, if we know the constitution of sulphuric acid, we may infer the constitution of this group. The fact that it is a residue of sulphuric acid is shown also

in the following way: By replacing one of the hydroxyl groups of sulphuric acid by an atom of chlorine, we obtain a compound of the formula $SO_2\begin{matrix}Cl\\OH\end{matrix}$, which, by simple treatment with water, is reconverted into sulphuric acid. There can be little doubt that the group SO_2OH of this chloride has exactly the same constitution as the corresponding group of the acid. But, if this chloride be allowed to act upon benzene, benzenesulphonic acid and hydrochloric acid are the products, the former having all the properties possessed by the benzenesulphonic acid formed by the action of sulphuric acid on benzene. The reaction takes place thus:

$$C_6H_6 + SO_2\begin{matrix}Cl\\OH\end{matrix} = C_6H_5.SO_2.OH + HCl.$$

Here, evidently, the group $SO_2.OH$ of the chloride takes the place of an atom of hydrogen in benzene.

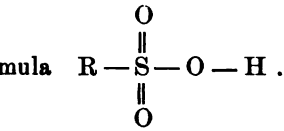
Assuming then the general formula $SO_2.OH$ for the group, it remains to decide in what manner the atoms of the sub-group SO_2 are united. Tne first question to be answered, and perhaps the only one that can be answered by experimental methods at present, is, whether in the compound containing the group SO_2, as, for example, $C_6H_5.SO_2.OH$, the sulphur is in direct combination with the hydrocarbon or not.

It has been shown that, when the sulphonic acids are reduced, they yield, as final products, the corresponding sulphydrates. Thus, $C_6H_5.SO_3H$ yields C_6H_5SH. Further, when the sulphydrates are oxidized, they yield sulphonic acids: $C_2H_5.SH$ yields $C_2H_5.SO_3H$, etc. The simplest interpretation of these results is found in the assumption that the sulphur is in direct combination with the hydrocarbon, as represented in the formulas:

$C_2H_5—S—H$, $C_2H_5—S—O_2—OH$ and $C_6H_5—S—H$, $C_6H_5 — S—O_2—OH$.

It is impossible to determine with any degree of certainty whether the two oxygen atoms (O_2) are both in direct combination with sulphur or not, though the opinion is now

commonly held that in the sulphuric acids the sulphur acts as a hexad and that the constitution is expressed by the general formula



Constitution of the Group NO_2.—When concentrated nitric acid acts upon hydrocarbons, etc., hydrogen is frequently replaced by the group NO_2, thus:

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Nitric acid.}}{NO_2OH} = \underset{\text{Nitrobenzene.}}{C_6H_5.NO_2} + H_2O$$

The reaction, as will be noticed, is similar to that which takes place when sulphuric instead of nitric acid is used. Just as in the former case we can assume that the group SO_3H is a residue of sulphuric acid, so in the latter case we may infer that the group NO_2 is a residue of nitric acid. The formula that we accept for nitric acid will show us the constitution of the group NO_2. Again, nitro compounds are formed by treating a chloride, bromide, or iodide of a hydrocarbon residue with silver nitrite, $AgNO_2$, the reaction taking place as follows:

$$\underset{\text{Ethyl iodide.}}{C_2H_5I} + AgNO_2 = \underset{\text{Nitroethane.}}{C_2H_5(NO_2)} + AgI.$$

It would appear from the latter reaction that the group NO_2 has the same constitution in the nitro derivatives that it has in nitrous acid; but this is in reality not the case, or, at least, certain facts seem to indicate clearly a dissimilarity of the groups.

There are two series of compounds of the same composition, but of different constitution, both of which contain the group NO_2. The members of one of these series are ethers of nitrous acid. If nitrous acid contains hydroxyl, then the ethers have the general constitution R—O—NO, in which R represents a hydrocarbon residue. The characterizing feature in the constitution of these ethers is the same as that which we find in all ethers, viz., the acid group is combined with the hydrocarbon residue by means of an *atom of oxygen*. That this is true of the ethers of nitrous acid is shown by the fact that, when nascent hydrogen acts upon them,

they yield the alcohols corresponding to the hydrocarbon residues which they contain, and at the same time ammonia. If the nitrogen atom had been directly united with the hydrocarbon residue, we would probably find it in combination with this residue after the above reduction. The decomposition which actually takes place may be represented thus:

Ether, R—O—NO, yields

$$\underset{\text{Alcohol.}}{R—O—H} \text{ and } \underset{\text{Ammonia.}}{H—N\begin{matrix}H\\H\end{matrix}}.$$

With the constitution assumed for the ether, it is evident that the formation of alcohol by the addition of hydrogen would necessitate the splitting off of the group containing nitrogen.

On the other hand, the second series of compounds are not ethers, but true substitution products. They consist of a hydrocarbon residue combined with the group NO_2 by means of the *nitrogen atom.* Their general constitution is expressed by the formula $R—NO_2$.

This conclusion is reached by considering the products of the reduction of nitro compounds. When treated with nascent hydrogen, they yield products known as amine bases, which are ammonia in which one hydrogen atom has been replaced by a hydrocarbon residue. The decomposition is represented as follows:

$$\underset{\text{Nitro product.}}{R—NO_2} + 6H = \underset{\text{Amine base.}}{R—NH_2} + 2H_2O.$$

In the product obtained in this case, it is evident that the nitrogen atom is in direct combination with the hydrocarbon residue, and hence we can assume that this kind of combination also existed in the original nitro compound.

Accepting the above formula for nitro compounds, it is difficult to see how they can be formed by the reaction with silver nitrite. For, if the hydrocarbon residue took the place occupied by the silver in the salt, it is plain that the product would be an ether, which, according to what has already been said, must have the formula R—O—NO. The product, however, is not an ether. Consequently, some other change besides that of an interchange of places by the silver atom and the hydrocarbon residue must be ac-

complished at the same time. Consequently, further, the group NO_2 in nitrous acid has a constitution differing from that of the group NO_2 of nitro compounds.

As to the respective constitutions of these two groups we see that in nitrous acid we have in all probability one hydroxyl. This gives us one oxygen atom combined with hydrogen on the one hand, and, on the other, with nitrogen, thus: H—O—N—. The only thing additional that is present in the molecule is an atom of oxygen, which it is safe to suppose is combined with nitrogen; whence we have the group —O—N—O or (—O—N=O) as the characteristic group of the acid and its derivatives. But the group of nitro compounds unites with residues by means of its nitrogen atom, as we have seen. Hence, we can conceive of two formulas for the group NO_2, viz., , in which the nitrogen is trivalent, and , in which the nitrogen is quinquivalent. It has not been found possible to decide which of these two formulas is the correct one. The latter, , is now more commonly accepted than the former.

Constitution of the Group NO.—There are two classes of compounds, both of which contain a group NO. They are the *nitroso* and the *isonitroso* compounds. The former may be prepared by treating with nitrous acid bodies which contain the so-called imido group NH, or those which contain the group CH. If, on the other hand, bodies which contain the group CH_2 are treated with nitrous acid, isonitroso compounds are formed. The fact that the nitroso compounds are converted into nitro compounds by oxidation, and into amido bodies, containing NH_2, points to an analogy with these substances. They are hence represented by the general formula R—NO.

The isonitroso compounds may be obtained by treating with hydroxylamine, NH_3O, bodies which contain the acetone or aldehyde group, CO. The reaction may be repre-

sented in two ways, according as we assume the presence of hydroxyl in hydroxylamine, or not:

$$X^{*} - CO + HH\,HNO = X-C\begin{matrix}H\\NO\end{matrix}$$

$$X - CO + H_2NOH = X-C-N-OH.$$

The results of the most recent experiments on the subject indicate that in the isonitroso compounds the relations between the elements is expressed by the formula X—C—N—OH, or X=C=N—OH. The experiments are still in progress.

Constitution of the Group NH_2.—Compounds which contain the group NH_2 are called *amido compounds.* The group is plainly a residue of ammonia and is univalent, having the constitution $-N\begin{matrix}H\\H\end{matrix}$. These compounds are readily obtained by the action of nascent hydrogen on nitro derivatives, the group NO_2 being hereby converted into NH_2. Amido substitution products have properties which ally them to ammonia, which fact is a further evidence of a similarity in the constitutions of the two. They have basic properties in the same sense that ammonia has basic properties, *i. e.*, they unite directly with all acids, forming salts. In addition to the above method of formation, we have also the action of aqueous ammonia upon chlorides, bromides, or iodides of hydrocarbon residues:

$$\underset{\text{Ethyl bromide.}}{C_2H_5Br} + NH_3 = \underset{\text{Ethylamine.}}{C_2H_5(NH_2)} + HBr.$$

This latter method indicates very clearly the intimate connection between amido compounds and ammonia.

Constitution of the Group NH.—Finally, there is a class of bodies called *imido compounds.* These contain the group NH, which is bivalent, and hence occupies the place of two hydrogen atoms. Like amido compounds, they may be

* X simply represents whatever the group may be in combination with.

considered as derived from ammonia by the replacement of two hydrogen atoms by hydrocarbon residues. The constitution of the group and of the compounds is readily understood. We have:

$$\left.\begin{matrix}C_2H_5Br\\C_2H_5Br\end{matrix}\right\} + NH_3 = \left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\} N + 2HBr\ .$$

2 mol. Ethyl bromide. — Diethylamine.

Constitution of the Groups N_2H_3 and N_2H_2.—The hydrazine compounds are closely allied to the amines. They bear the same relation to the hypothetical body, N_2H_4, that the amines bear to ammonia. Diethylhydrazine $(C_2H_5)_2N_2H_2$, may be prepared by starting from diethylamine $(C_2H_5)_2NH$. When this is treated with nitrous acid a nitroso compound $(C_2H_5)N(NO)$, is formed. By reduction the nitroso compound may be converted into the corresponding amido compound $(C_2H_5)_2N—NH_2$, which is diethylhydrazine.

The various classes of chemical compounds which we have thus studied are the principal classes with which we have to deal. There are a few other classes, among which may be mentioned the so-called *mustard oils*, the *diazo compounds*, and the *quinones*. These will be considered later, in connection with those better known compounds with which they are most closely allied.

In classifying compounds we have distinguished between general classes and their substitution products. This distinction is generally justified, though, in a certain sense, even those compounds which belong to the general classes are substitution products, or, at least, may be considered as such. This is particularly the case with the compounds of carbon, all of which may be looked upon as derived from certain hydrocarbons by the introduction of various groups. Thus the alcohols are derived from hydrocarbons by replacing hydrogen by hydroxyl, OH; the acids by replacing hydrogen by carboxyl, CO.OH, etc. Speaking, then, of all the groups which have been studied as substituting groups, the general statement may be made that: In all substituting groups the characterizing element or elements may be re-

placed by another or others of the same general character. Thus, as we have already seen, oxygen may be replaced by sulphur. Further, sulphur may, in some cases, be replaced by selenium or tellurium; nitrogen may be replaced by phosphorus, etc. Thus we get new compounds, but the constitution of these is the same as that of those from which they are derived, and hence they require no separate treatment n this place.

II.

SPECIAL STUDY OF THE CONSTITUTION OF CHEMICAL COMPOUNDS.

FROM the general considerations of the preceding section, the constitution of the majority of compounds will be directly understood. In the following section, the constitution of individual compounds will be considered, in so far as any special consideration of them is necessary. Here the compounds of carbon again will require our attention, because more is known concerning their constitution than is known concerning other compounds. It will be found that the same atoms may frequently be arranged in different ways, giving rise to different compounds.

Isomerism.—There are two ways in which bodies may contain the same elements in the same proportions by weight, and still be different bodies:

1. The atoms or groups, composing the body, may be arranged differently in the molecule, as above stated. Thus, we have ammonium cyanate, $CN(ONH_4)$, and urea or carbamide, $CO\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix}$. These bodies contain the same atoms in the same number in their molecules. Such bodies are called *metameric.*

2. Bodies may have the same composition, but have different molecular weights. Thus, we have acetylene, C_2H_2, and benzene, C_6H_6. Such bodies are called *polymeric.*

COMPOUNDS NOT CONTAINING CARBON.

The compounds which the univalent elements, hydrogen, chlorine, bromine, iodine, fluorine, sodium, potassium, lithium, cæsium, rubidium, silver, form with each other ap-

pear to have the simplest constitution of which we have any conception. They require no study here.

Compounds of Chlorine, etc., with Oxygen, and with Oxygen and Hydrogen.—Hydrogen peroxide has the empirical formula H_2O_2. If in this compound the oxygen is bivalent, the arrangement of the atoms can be most readily imagined to be in accordance with the formula H—O—O—H. There is, indeed, no independent proof of the correctness of this formula, but no other formula expresses the constitution at all satisfactorily, and hence this is accepted as correct.

The acids which chlorine forms with oxygen and hydrogen are most frequently considered as represented by the following formulas:

Cl—O—H,	hypochlorous acid,
Cl—O—O—H,	chlorous acid,
Cl—O—O—O—H,	chloric acid,
Cl—O—O—O—O—H,	perchloric acid;

and the compounds of chlorine with oxygen alone by the following formulas:

Cl—O—Cl,	hypochlorous anhydride,
Cl—O—O—O—Cl,	chlorous anhydride,
Cl—O—O—O—O—Cl,	chlorous-chloric anhydride.

The corresponding compounds of bromine, iodine, and fluorine, as far as they are known, are represented by corresponding formulas. It must be confessed that these formulas are by no means well established, and it is very possible that, when the compounds themselves shall have been studied more carefully, they will be found to be incorrect. Indeed there is a tendency now to consider the chlorine in these compounds as polyvalent, the following formulas being based upon this view:

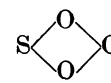
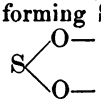
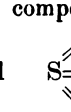
$$Cl(=O)-O-H, \quad Cl(=O)(=O)-O-H \quad \text{and} \quad O=Cl(=O)-O-H.$$

It is claimed that, while chlorine is undoubtedly only univalent with reference to hydrogen, it may be heptavalent with reference to oxygen.

Compounds of Sulphur, etc., with Oxygen, and with Oxygen and Hydrogen.—Sulphur forms a number of compounds with oxygen and hydrogen, some of which have been carefully studied. The compounds with oxygen alone are sulphur dioxide, SO_2, and sulphur trioxide, SO_3. If, in these compounds, both the sulphur and the oxygen are bivalent, we have the following possible formulas:

For SO_2, , , —S—O—O—;

For SO_3, , , —S—O—O—O—.

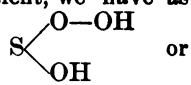
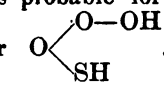
As is plain, all the formulas except and  represent the compounds as unsaturated. Now SO_2 conducts itself like an unsaturated compound; it combines directly with chlorine, forming the product SO_2Cl_2, and with oxygen, forming SO_3, so that it seems possible that the formula  or S—O—O— may in reality express its constitution. Again, some chemists consider sulphur quadrivalent or sexivalent in these compounds, which would give the formulas and  .

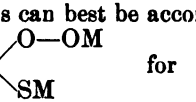
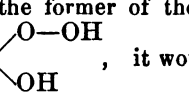
These are perhaps the most commonly accepted formulas, though the reasons for accepting them are not very good ones.

The acids of sulphur are the following:

H_2SO_3,	sulphurous acid.
H_2SO_4,	sulphuric acid.
$H_2S_2O_7$,	pyrosulphuric acid.
$H_2S_2O_3$,	hyposulphurous or thiosulphuric acid.
$H_2S_2O_6$,	hyposulphuric or dithionic acid.
$H_2S_3O_6$,	trithionic acid.
$H_2S_4O_6$,	tetrathionic acid.
$H_2S_5O_6$,	pentathionic acid.

Sulphurous Acid, H_2SO_3.—Derivatives only of this acid are known, as the salts and ethers. From a study of these derivatives, conclusions have been drawn concerning the constitution of the acid itself. The constitution of sulphurous acid is expressed by very different formulas by those who consider sulphur as bivalent, and those who consider that it may and does act as quadrivalent or sexivalent. Up to the present, no conclusive evidence for either view has been furnished. If we assume that it is bivalent, we are led to certain conclusions with regard to the constitution of the acid. We may make this assumption, without interfering with our main object, which is more particularly to show the methods of thought and experiment that lie at the foundation of constitutional formulas in general.

If then sulphur is bivalent, we have as probable formulas for sulphurous acid  or  .

For some time the latter formula was accepted, in consequence of the fact that the sulphonic acids are so readily formed from salts of sulphurous acid. We have seen that in these acids, the group SO_3H is combined with hydrocarbon residues by means of the sulphur atom. Now, as the group SO_3H can apparently be obtained from sulphites, such a constitution was assigned to the latter as to make the connection between them and the sulphonic acids clear. This can best be accomplished if we accept the formula  for the sulphites. If the metal which is in combination with sulphur in this formula be replaced by a hydrocarbon residue, the latter would be in combination with sulphur also. On the other hand, if we accept the former of the two formulas above proposed, viz.,  , it would appear difficult to obtain sulphonic acids from sulphites by a simple interchange of atoms or groups.

Sulphuric Acid, H_2SO_4.—By means of reactions which have been discussed, the presence of two hydroxyl groups

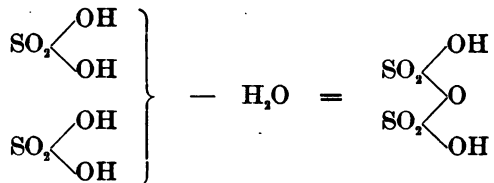
in sulphuric acid may be inferred. We thus have the formula $SO_2\begin{matrix}OH\\OH\end{matrix}$. We cannot, however, by experiment determine the constitution of the group SO_2. It is now commonly believed to have the constitution expressed by the formula O=S=O, and sulphuric acid itself is regarded as $O=S(-O-H)_2$, in which the sulphur is sexivalent.

There are, however, some facts known which cannot well be brought in harmony with this view. According to the formula of sulphuric acid just given, the existence of only one mono-ethyl ether of the acid appears possible, viz., $O=S(-O-C_2H_5)(-O-H)$. It could apparently make no difference whether the ethyl replaced one hydrogen or the other. But two ethyl ethers have been described. One of these is formed as follows: By the action of the chloride of phosphorus on sulphuric acid, sulphuryl oxychloride, $SO_2\begin{matrix}OH\\Cl\end{matrix}$, is obtained. Now, if sulphuryl oxychloride is treated with ethylene, a compound, $SO_2\begin{matrix}OC_2H_5\\Cl\end{matrix}$, is formed by direct addition. An isomeric substance is said to be formed when sulphuryl oxychloride is treated with alcohol.

Assuming that there really are two monoethyl ethers of sulphuric acid, it is difficult to explain this if sulphur is sexivalent in the acid. On the other hand, if the sulphur is bivalent, and the acid has the constitution HO—S—O—O—OH, then it is possible to get two monoethyl ethers from it, viz.:

$$C_2H_5O—S—O—O—OH$$
$$HO—S—O—O—OC_2H_5.$$

Pyrosulphuric Acid, $H_2S_2O_7$.—Pyrosulphuric acid is a partial anhydride of sulphuric acid obtained by abstracting one molecule of water from two molecules of the acid:



2 mol. Sulphuric acid. Pyrosulphuric acid.

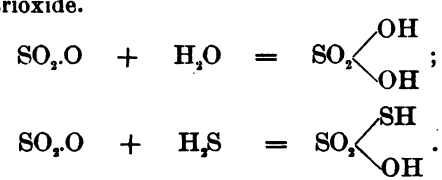
The general statements made in connection with the subject of anhydrides contain the proofs for the above formula. Of course, the groups SO_2 contained in this anhydride are supposed to have the same constitution that they have in sulphuric acid.

Hyposulphurous or Thiosulphuric Acid, $H_2S_2O_3$.—This acid is usually considered as sulphuric acid in which one of the hydroxyl groups has been replaced by the group SH, thus:

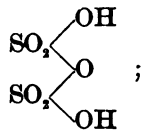
Sulphuric acid. Thiosulphuric acid.

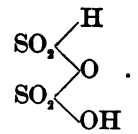
This formula is rendered probable by the fact that thiosulphuric acid may be obtained from sulphuric acid by treating the latter with phosphorus sulphide. The action of the latter reagent consists in replacing oxygen by sulphur. And the oxygen of the hydroxyl group is, in general, more susceptible to the influence of reagents than that contained in the group SO_2.

Further, thiosulphuric acid is obtained by allowing hydrogen sulphide to act upon sulphur trioxide, just as sulphuric acid is obtained by allowing water to act upon sulphur trioxide.

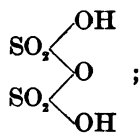


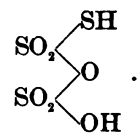
Dithionic Acid, $H_2S_2O_6$, is considered as related to pyrosulphuric acid, thus:


Pyrosulphuric acid.

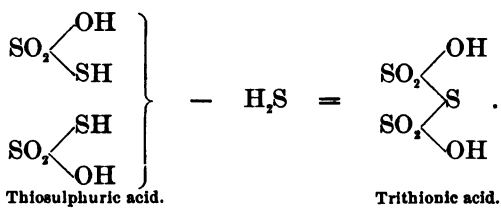

Dithionic acid.

Trithionic Acid, $H_2S_3O_6$, may be considered as derived from pyrosulphuric acid in the same way that thiosulphuric acid is derived from sulphuric acid, thus:


Pyrosulphuric acid.

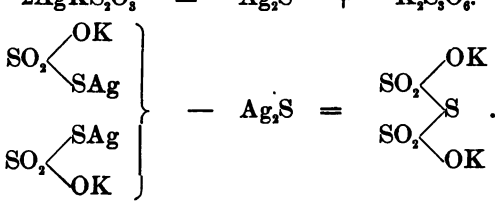

Trithionic acid.

Or, it may be that trithionic acid is an anhydride of thiosulphuric acid:


2 mol. Thiosulphuric acid. Trithionic acid.

The latter view is rendered probable by the fact that trithionates are formed when double salts of thiosulphuric acid are boiled with water. The reaction takes place according to the following equation:

$$2AgKS_2O_3 = Ag_2S + K_2S_3O_6.$$

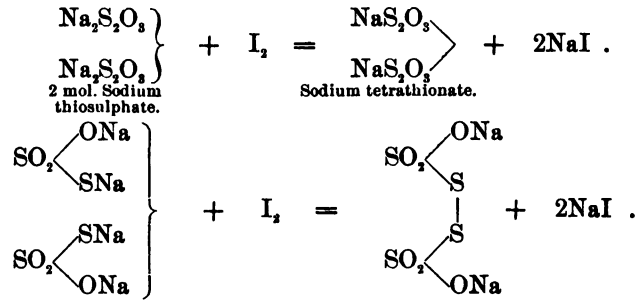


When potassium trithionate is boiled with potassium sulphide, potassium thiosulphate is formed:

$$K_2S_3O_6 + K_2S = 2K_2S_2O_3.$$

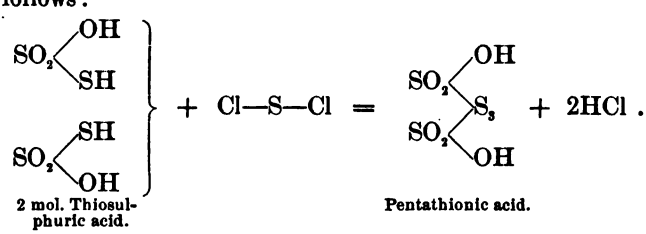
This reaction also indicates an intimate relation between thiosulphuric and trithionic acids.

Tetrathionic Acid, $H_2S_4O_6$, is obtained by the action of iodine on sodium thiosulphate, thus:



Hence, the formula of the acid from which the latter salt is derived is accepted for tetrathionic acid.

Pentathionic Acid, $H_2S_5O_6$, is obtained by treating barium thiosulphate with sulphur bichloride, SCl_2. The latter compound probably has the constitution Cl—S—Cl; consequently, the reaction may be interpreted most readily as follows:



The corresponding acids of selenium and tellurium, as far as they are known, are represented by similar formulas.

Compounds of Nitrogen with Oxygen, and with Oxygen and Hydrogen.—Nitrogen forms with oxygen the following compounds:

N_2O, nitrous oxide or nitrogen monoxide.
NO or N_2O_2, nitrogen dioxide.
N_2O_3, nitrogen trioxide.
NO_2 or N_2O_4, nitrogen tetroxide.
N_2O_5, nitrogen pentoxide.

We know practically nothing about the arrangement of the atoms in these compounds.

The constitution of *nitrogen monoxide* is usually expressed by the formula $\begin{matrix} N{=}N \\ \diagdown\diagup \\ O \end{matrix}$

Nitrogen dioxide is expressed by —N=O. It is unsaturated. The readiness with which it combines with oxygen and chlorine indicates its unsaturated condition.

Nitrogen tetroxide is expressed by —O—N=O or $\begin{matrix} O \\ \| \\ N- \\ \| \\ O \end{matrix}$, and is also unsaturated.

As regards *nitrous acid*, HNO_2, we can only say that it probably contains hydroxyl (OH), and that its constitution is expressed by the formula ON—OH, or O=N—O—H. It is not known whether in *nitric acid* the nitrogen is trivalent or quinquivalent. If it is trivalent, the acid is $HO{-}N\begin{matrix} O \\ \diagup\diagdown \\ O \end{matrix}$; if it is quinquivalent, the acid is $\begin{matrix} O \\ \| \\ N{-}O{-}H \\ \| \\ O \end{matrix}$.

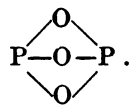
It makes little difference which of the formulas we use at the present time, though it is better to use neither, as the formula NO_2—OH expresses all that we know in regard to the acid.

Hydroxylamine, H_3NO.—This substance conducts itself like ammonia in many respects, and is hence regarded as a substituted ammonia. It is probable that its constitution is expressed by the formula $\begin{matrix} H \\ \diagup \\ N{-}H \\ \diagdown \\ OH \end{matrix}$.

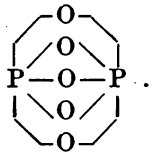
Compounds of Phosphorus with Oxygen, and with Oxygen and Hydrogen.—Phosphorus forms two oxides, viz.:

P_2O_3,	phosphorus trioxide.
P_2O_5,	phosphorus pentoxide.

The former is usually considered as derived from trivalent phosphorus, and to it is consequently given the formula



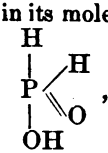
The latter, however, is considered as derived from quinquivalent phosphorus, and to it is given the formula



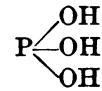
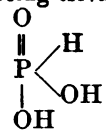
These formulas are purely hypothetical.

There are several acids of phosphorus, viz.:

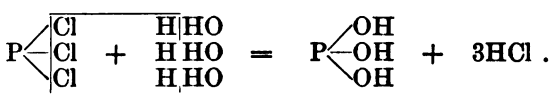
H_3PO_2,	hypophosphorous acid.
H_3PO_3,	phosphorous acid.
H_3PO_4,	phosphoric acid.
$H_4P_2O_7$,	pyrophosphoric acid.
HPO_3,	metaphosphoric acid.

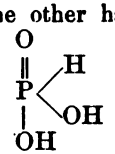
Hypophosphorous Acid, H_3PO_2, is monobasic, and hence only one hydroxyl group is assumed as present in its molecule. This gives the formula $H_2PO.OH$ or  , in which the phosphorus atom is quinquivalent.

Phosphorous Acid, H_3PO_3.—In regard to the constitution of this acid, two views are held. According to the

first, the formula of the acid is  , the phosphorus being trivalent. According to the second, the formula is  , the phosphorus being quinquivalent.

If the former formula is correct, the acid ought to be tribasic. In most of its salts, however, it is only bibasic. Still, ethers are known which are evidently derived from a tribasic acid, as, for instance, $PO_3(C_2H_5)_3$; and it has, further, recently been shown that a salt of the acid exists in which there are three atoms of a univalent metal to the molecule. These latter facts would lead to the formula $P(OH)_3$. The fact also, that phosphorous acid is produced by simply treating phosphorus trichloride with water, is in accordance with this formula. We have

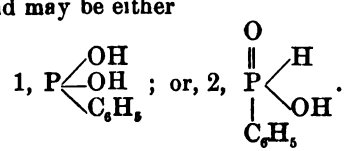


On the other hand, the following facts speak for the formula  :

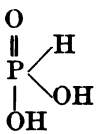
When benzene is treated with phosphorus trichloride, under appropriate conditions, the following reaction takes place:

$$PCl_3 + C_6H_6 = PCl_2(C_6H_5) + HCl.$$

When the main product, phosphenyl chloride, is treated with water, the chlorine is eliminated, and a compound of the composition $PO_2H_2(C_6H_5)$ is formed. The formula of this compound may be either



If the latter is the formula, then we may conclude that the constitution of phosphorous acid is similar, *i. e.*,



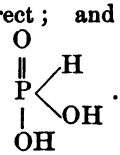
If formula 1 is correct, then, by the action of phosphorus pentachloride upon the compound, the following reaction ought to take place:

I. $P(OH)_2C_6H_5 + 2PCl_5 = PCl_2(C_6H_5) + 2(POCl_3) + 2HCl.$

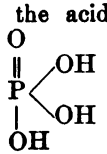
If, however, formula 2 is correct, then, under the same conditions, the following reaction would take place:

II. $OPH(OH)C_6H_5 + 2PCl_5 = OPCl_2(C_6H_5) + POCl_3 + PCl_3 + 2HCl.$

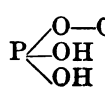
In the former case, phosphenyl chloride, $PCl_2(C_6H_5)$, would be formed; in the latter, phosphenyl oxychloride, $POCl_2(C_6H_5)$. Direct experiments showed that phosphenyl oxychloride, phosphorus oxychloride, and phosphorus trichloride are formed, and consequently the formula $OPH(OH)C_6H_5$ is correct; and phosphorous acid by analogy is $OPH(OH)_2$ or



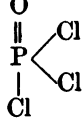
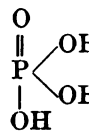
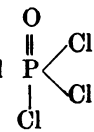
Phosphoric Acid, H_3PO_4.—This acid is tribasic, and hence three hydroxyl groups are assumed to be present in it. From this follows directly the formula $PO(OH)_3$. The question still remains whether the phosphorus is quinquivalent or trivalent in the acid. In the former case, the formula would be



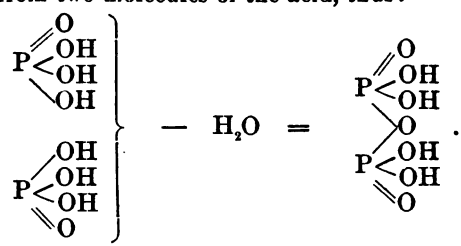
; in the latter,



: Phosphoric acid is obtained by treating

phosphorus oxychloride with water. If the oxychloride is  , then we would expect phosphoric acid to have the former of the two formulas given. If the oxychloride is , then the acid has probably the latter of the two formulas given. The formulas  and  are usually accepted, though without positive proofs of their correctness.

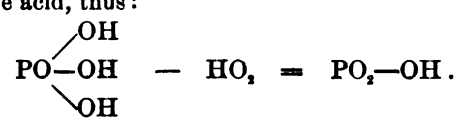
Pyrophsophoric Acid, $H_4P_2O_7$.—This is a partial anhydride of phosphoric acid formed by abstracting one molecule of water from two molecules of the acid, thus:



2 mol. Phosphoric acid. Pyrophosphoric acid.

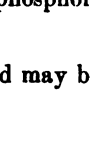
The constitution is readily understood by the aid of the general remarks on the subject of anhydrides.

Metaphosphoric Acid, HPO_3.—The composition of this acid is similar to that of nitric acid, HNO_3. It is, like pyrophosphoric acid, a partial anhydride of phosphoric acid, formed by abstracting one molecule of water from one molecule of the acid, thus:



Phosphoric acid. Metaphosphoric acid.

Metaphosphoric acid is probably analogous to nitric acid, and may be



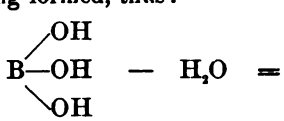
The relations between phosphoric acid and its anhydrides are shown by the following tables:

$2(H_3PO_4) - H_2O = H_4P_2O_7$,	pyrophosphoric acid.
$2(H_3PO_4) - 2H_2O = 2HPO_3$,	metaphosphoric acid.
$2(H_3PO_4) - 3H_2O = P_2O_5$,	phosphoric anhydride.

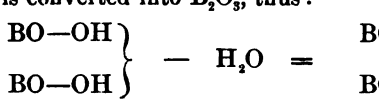
$P_2O_5 + H_2O = 2HPO_3$,	metaphosphoric acid.
$P_2O_5 + 2H_2O = H_4P_2O_7$,	pyrophosphoric acid.
$P_2O_5 + 3H_2O = 2H_3PO_4$,	phosphoric acid.

Arsenic, antimony, and bismuth form some compounds analogous to those of phosphorus here described. Much of what has been said of the constitution of the latter probably holds good for the constitution of the former.

Compounds of Boron with Oxygen and with Oxygen and Hydrogen.—Boron forms only one oxide, viz., B_2O_3, known as boron trioxide. The acid to which it corresponds is $B(OH)_3$. When boric acid, $B(OH)_3$, is heated for some time at 100°, it loses a molecule of water, a partial anhydride being formed, thus:



When this anhydride is heated to a much higher temperature, it is converted into B_2O_3, thus:



Compounds of Silicon with Oxygen and with Oxygen and Hydrogen.—Silicon bears a close analogy to carbon in some respects. It usually acts as a quadrivalent element, as is seen in the compound SCl_4. When this chloride is treated with water, we would expect as a product $Si(OH)_4$, which may be considered as the normal acid of silicon. It appears to be possible to obtain this acid, but it is very unstable. It loses water easily, and thus yields a partial anhydride, SiO_3H_2, thus:

$$Si(OH)_4 - H_2O = SiO_3H_2 = SiO(OH)_2.$$

This compound is usually called silicic acid, as from it most of the silicates are derived.

If heated, this acid yields complicated polysilicic acids, which, in their turn, are partial anhydrides. They are formed by the union of two or more molecules of silicic acid and the abstraction of varying amounts of water from them. Examples of such polysilicic acids are:

$$Si_2O_3(OH)_2,\ Si_3O_4(OH)_4,\ Si_3O_5(OH)_2,\ Si_4O_7(OH)_2,\ \text{etc.},$$

some of which are found in nature, as opal, hydrophane, etc. As final product of the action of heat on silicic acid, we have silicon dioxide, SiO_2.

Salts.—The constitution of the most important acids being thus understood, that of the salts, in general, requires no special consideration; for we have seen that the salts are very simple derivatives of the acids. There are a few metals and groups, however, which have the property of yielding peculiar salts, and these require a brief consideration.

Ammonium Salts.—When ammonia, NH_3, acts upon any acid, a salt is formed by direct addition, thus:

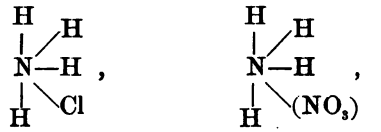
$$NH_3 + HCl = \underset{\text{Ammonium chloride.}}{(NH_4)Cl}$$

$$NH_3 + HNO_3 = \underset{\text{Ammonium nitrate.}}{(NH_4)NO_3}$$

$$2NH_3 + H_2SO_4 = \underset{\text{Ammonium sulphate.}}{(NH_4)_2SO_4}.$$

The salts thus formed are similar to the salts of potassium, sodium, etc., KCl, KNO_3, K_2SO_4, etc. They conduct

themselves like true metallic salts. Hence the group NH_4, which is contained in them, is supposed to play the part of a metal, and to it the name ammonium is given. Accordingly, the salts are called ammonium salts. These have been referred to incidentally, under the head of valence. It was shown that in them the nitrogen is probably quinquivalent. The formulas of the above salts are, accordingly:



Salts of Copper and Mercury.—Copper and mercury form two series of salts, of which the following are examples:

Cu_2Cl_2, $CuCl_2$	Hg_2Cl_2, $HgCl_2$
$Cu_2(NO_3)_2$, $Cu(NO_3)_2$	$Hg_2(NO_3)_2$, $Hg(NO_3)_2$
$Cu_2(SO_4)$, $Cu(SO_4)$	$Hg_2(SO_4)$, $Hg(SO_4)$.

If we determine the formulas of the two chlorides of mercury by the aid of the specific gravity of their vapors, we are led to HgCl and $HgCl_2$. According to these formulas, mercury is bivalent, and the compound HgCl is unsaturated. It has been supposed, however, that the formula of the chloride HgCl in the solid condition is in reality Hg_2Cl_2, and that it has the constitution $\begin{matrix} HgCl \\ | \\ HgCl \end{matrix}$. The group $\begin{matrix} Hg \\ | \\ Hg \end{matrix}$ is bivalent as well as the mercury atom itself, and thus the above two series of salts are explained. The same explanation is given for the *corresponding salts of copper.*

A large number of compounds are known which are derived from salts of ammonium and contain copper and mercury. They seem to consist of ammonium salts, in which a portion of the hydrogen of the ammonium groups has been replaced by copper or mercury, thus:

$Hg_2Cl_2 + 2NH_3 = \begin{matrix} NH_3Hg_2Cl \\ NH_3 \end{matrix}$, Dimercury diamidochloride.

$NO_3.NH_2Hg_2$, Dimercuryamine nitrate.

These formulas are purely hypothetical.

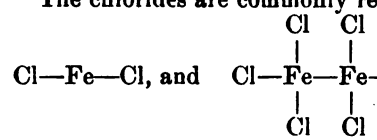
Similar compounds are formed with other metals, particularly with cobalt, which furnishes a very large number of interesting substances of this kind. These are too complicated and too little understood to permit the drawing of positive conclusions concerning their constitution. Their study promises interesting results.

Salts of Iron and Chromium.—Iron and chromium form two series of salts, which should probably be represented by the formulas:

$FeCl_2$,	Fe_2Cl_6.
$Fe(NO_3)_2$,	$Fe_2(NO_3)_6$.
$FeSO_4$,	$Fe_2(SO_4)_3$.

$CrCl_2$,	Cr_2Cl_6.
$Cr(NO_3)_2$,	$Cr_2(NO_3)_6$.
$CrSO_4$,	$Cr_2(SO_4)_3$.

The chlorides are commonly represented by the formulas



Cl—Fe—Cl, and Cl—Fe—Fe—Cl, according to which iron acts either as a bivalent or a quadrivalent element.

Salts of Aluminium.—The chloride of aluminium, Al_2Cl_6, is regarded as analogous to that of iron. Al_2Cl_6 and aluminium is quadrivalent.

Metal Acids.—The four metals, iron, chromium, manganese, and aluminium, form hydroxides of the general formula MO.OH, which conduct themselves like weak acids, forming salts with some metals. Thus, we have AlO.OK and AlO.ONa, salts of the hydroxide AlO.OH.*

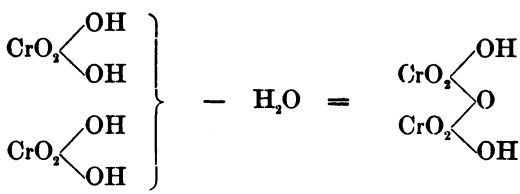
Iron, manganese, and chromium yield acids of the general

* Of course, if the chloride is Al_2Cl_6, this compound is probably $Al_2O_2(OH)_2$, and the salts have a corresponding composition.

formula MO_4H_2. Thus, we have FeO_4H_2, MnO_4H_2, and CrO_4H_2. These acids are analogous to sulphuric acid, H_2SO_4, and a close resemblance is noticed between the salts of sulphuric acid and those of chromic acid, which is the best known of the three above-named acids.

In the absence of satisfactory evidence regarding the constitution of these acids, the only formulas which we are at all justified in using are those which have the general form $MO_2(OH)_2$.

A very important salt of chromium is that known as potassium bichromate or pyrochromate. The formula of this salt is $Cr_2O_7K_2$. It may be regarded as the salt of an acid which is analogous to pyrosulphuric acid, and derived from chromic acid by the abstraction of water, thus:



2 mol. Chromic acid. Pyrochromic acid.

Neither chromic acid itself nor pyrochromic acid can be prepared in the free condition. The group CrO_2 does not appear to be capable of holding hydroxyl in combination, so that salts of the formula $CrO_2(OH)(OM)$ are not known.

An acid of manganese furnishes salts of the general formula MnO_4M. No positive assertion can be made in regard to the constitution of this acid, except that it is monobasic, and hence it probably contains one hydroxyl group. This gives the formula MnO_3—OH, but the group MnO_3 remains unexplained.

Compounds of Uranium.—In connection with the subject of bases it was mentioned that uranium forms a peculiar set of salts in which the bivalent group UO_2 is supposed to take the place of the hydrogen of the acids. Thus, we have the

following compounds, UO_2Cl_2, $UO_2(NO_3)_2$, $UO_2(SO_4)$, etc., which can be most readily explained by assuming that in them the group UO_2 acts like a bivalent metal.

Uranium, further, forms salts of the general formula $U_2O_7M_2$, which may be regarded as derived from a complex hydroxide, $U_2O_7H_2 = O\begin{<}(UO_2)OH.\\(UO_2)OH.\end{>}$

This formula is, however, only hypothetical.

Constitution of Carbon Compounds.

As has already been stated, a great deal more is known concerning the constitution of carbon compounds than of those compounds which do not contain carbon. Having considered the general constitution of the classes of compounds with which we meet, it remains to study those changes which the members of the different classes can undergo without losing their main characteristics. We shall find that the compounds of carbon may be divided into a few distinct groups; that each of these groups may be referred to some fundamental substance of which all the other members of the group may be regarded as derivatives. The principal groups are: the Marsh-gas, or Methane compounds, also called Fatty Bodies; the Benzene compounds, also called Aromatic Bodies; the Naphthalene compounds; and the Anthracene compounds. The first two groups comprise by far the largest number of carbon compounds.

Methane Derivatives. (Fatty Bodies.)

Bodies derived from the Hydrocarbons C_nH_{2n+2}.

The constitution of methane has been considered above (see *ante*, p. 119.) It was shown that by the linking of carbon atoms to each other the possibility is given for the formation of an homologous series, the members of which differ from each other by CH_2, or a multiple of this. The following members of the series have been particularly well studied.

Methane,	CH_4.	Pentane,	C_5H_{12}.
Ethane,	C_2H_6.	Hexane,	C_6H_{14}.
Propane,	C_3H_8.	Heptane,	C_7H_{16}.
Butane,	C_4H_{10}.		

In speaking of substitution products it was stated that, according to the views now held concerning constitution, only one mono-substitution product of methane can exist. The same thing is true of other substitution products in which more than one substituting group is present. Further, we can only conceive of one variety of methane itself, and only one variety has ever been observed.

Derivatives of Ethane, C_2H_6.—According to the prevailing views, only one variety of this hydrocarbon can exist, and only one variety has been observed. Of its mono-substitution products also, only one variety can exist, and only one variety has been observed.

Of the bi-substitution products, however, two varieties are possible, as may be seen by comparing the following formulas:

In the first, the substituting groups are in combination with different carbon atoms; in the second, both substituting groups are in combination with the same carbon atom.

A number of compounds are known belonging to the classes of which these are the general formulas. X may represent any of the substituting groups with which we have had to deal; or the class groups CH_2OH, COH, COOH, etc.

The simplest of these are the bichlorine derivatives, one of which is $CHCl_2.CH_3$, and the other $CH_2Cl.CH_2Cl$. The first is called ethylidene chloride, the second, ethylene chloride. The constitution of these compounds is deduced from the following facts:

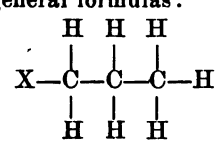
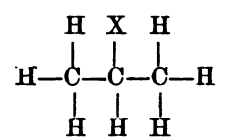
Ethylidene chloride is produced by the action of phosphorus pentachloride on aldehyde. We have seen that

an aldehyde contains the group · Ordinary aldehyde is · As in the reaction with phosphorus chloride, the oxygen is simply replaced by chlorine, the constitution $CH_3—CHCl_2$ follows for ethylidene chloride. It follows, further, that $CH_2Cl.CH_2Cl$ must be the formula of ethylene chloride.

Other compounds closly related to these two chlorides will be considered under the heads of ethylene, bibasic acids, etc.

Derivatives of Propane, C_3H_8.—Propane may be considered as a mono-substitution product of ethane, derived from the latter by replacing an atom of hydrogen with CH_3. From what was said above, it will, hence, be seen that only one variety of propane can exist; only one variety has been observed.

Under the head of substitution products, it has been shown that there are two kinds of carbon atoms, and, consequently, two kinds of hydrogen atoms in propane; and hence, further, that two different mono-substitution products may be obtained from this hydrocarbon. These have the general formulas:

 and  .

The compounds represented by the first formula are known as propyl compounds; those represented by the second formula as isopropyl or pseudopropyl compounds.

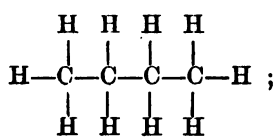
The two alcohols, normal propyl alcohol— $CH_3.CH_2.CH_2OH$, and isopropyl or pseudopropyl alcohol— $CH_3.CHOH.CH_3$, are the starting-points for the preparation of the two series of isomeric propyl compounds. As the former is a primary alcohol, it follows, from what has been said concerning these alcohols, that it must contain the group CH_2OH. This can only be the case if the hydroxyl group is in combination with one of the terminal carbon atoms. Consequently, the above constitution is assigned to

it. By replacing the hydroxyl by chlorine, bromine, iodine, cyanogen, etc., corresponding derivatives are obtained.

Isopropyl alcohol is obtained from acetone, and, being a secondary alcohol, contains the group CH.OH. Consequently, its hydroxyl is in combination with the central carbon atom of propane. By replacing the hydroxyl with chlorine, bromine, iodine, cyanogen, etc., corresponding isopropyl derivatives are obtained.

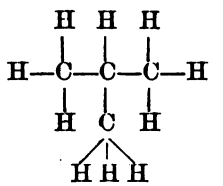
Derivatives of Butane, C_4H_{10}.—Butane may be considered as a mono-substitution product of propane; consequently, two varieties must be possible, one of which would have the formula:

I.



while the other would have the formula:

II.

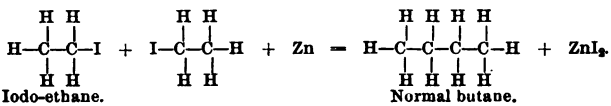


As a matter of fact, two varieties of butane are known to us, viz., normal butane and isobutane or trimethylmethane.*

* The simplest names in use for the members of the methane series of hydrocarbons are those in which the members are all regarded as derivatives of methane. Thus, ethane is called methyl-methane, $C\begin{cases}CH_3\\H\\H\\H\end{cases}$; propane is ethyl-methane, $C\begin{cases}C_2H_5\\H\\H\\H\end{cases}$; normal butane is propyl-methane, $C\begin{cases}C_3H_7\\H\\H\\H\end{cases}$; isobutane is trimethyl-methane $C\begin{cases}CH_3\\CH_3\\CH_3\\H\end{cases}$ etc.

The former has the constitution represented by formula I., above; the latter that represented by formula II.

Proofs.—The proof of the formula of normal butane is the same in nature as that given for ethane (see p. 121). It is formed by the action of zinc or sodium on iodo-ethane, according to the equation:

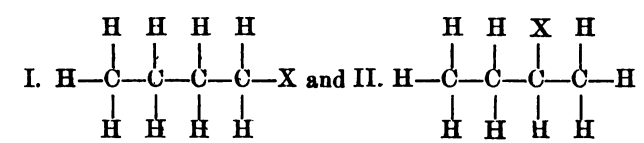


$$2\,C_2H_5I + Zn = C_4H_{10} + ZnI_2.$$

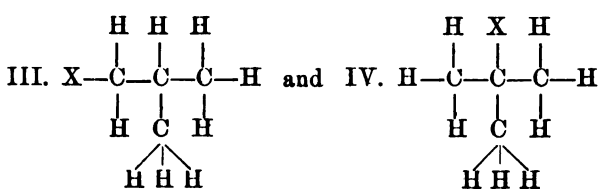
Of course we here assume that we know the formula of iodo-ethane, but we have already presented good grounds for this assumption. Starting with this formula, we are led very easily to the above formula of normal butane.

Trimethylmethane is obtained from pseudobutyl iodide, the constitution of which is known to be $CH_3\diagdown\!\!\diagup CI—CH_3$. When the iodine is replaced by hydrogen, the hydrocarbon is the product. (See Pseudobutyl Alcohol.)

Of normal butane, two kinds of simple substitution products are possible of the general formulas:



Of trimethylmethane, there are also two kinds possible, of the formulas:



Representatives of all four kinds of substitution products are known. The principal of these are the alcohols.

1. Normal butyl alcohol (propyl carbinol),*

$$CH_3.CH_2.CH_2.CH_2.OH.$$

2. Secondary butyl alcohol (methyl-ethyl carbinol),

$$CH_3.CH.OH.CH_2.CH_3.$$

3. Isobutyl alcohol (isopropyl carbinol),

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\!CH.CH_2.OH.$$

4. Tertiary butyl alcohol (trimethyl carbinol),

$$CH_3.C.OH\!<\!\!\begin{matrix} CH_3 \\ CH_3 \end{matrix}.$$

From each of these alcohols the corresponding chlorides, bromides, etc., can easily be obtained.

Proofs.—Normal butyl alcohol is obtained indirectly from normal butyric acid, the constitution of which is known.

Secondary butyl alcohol is converted by oxidation into ethyl-methyl acetone, $C_2H_5—CO—CH_3$. It is, hence, a secondary alcohol, and its constitution is that expressed above.

Isobutyl alcohol is converted into isobutyric acid by oxidation. The constitution of the acid is known, and hence also that of the alcohol.

* The simplest names for the alcohols are those in which they are regarded as derivatives of methyl alcohol or carbinol. Thus ethyl alcohol is methyl carbinol, $C\begin{cases} CH_3 \\ H \\ H \\ OH \end{cases}$; normal propyl alcohol is ethyl carbinol, $C\begin{cases} C_2H_5 \\ H \\ H \\ OH \end{cases}$; secondary propyl alcohol is dimethyl carbinol, $C\begin{cases} CH_3 \\ CH_3 \\ H \\ OH \end{cases}$, etc.

Tertiary butyl alcohol is a tertiary alcohol, and hence, from what has been said regarding these alcohols, it follows that it contains the group COH. It is prepared by treating acetyl chloride, $CH_3.COCl$, with zinc methyl, $Zn(CH_3)_2$, and hence contains three groups CH_3. The only formula which is in accordance with these facts is that above assigned to the alcohol.

Derivatives of Pentane, C_5H_{12}.—Three varieties of pentane may exist. These have the formulas:

1. $H_3C.CH_2.CH_2.CH_2.CH_3$.

2. $H_3C.CH_2.CH(CH_3)_2$.

3. $C(CH_3)_4$.

All three of these compounds are known. The first is *normal pentane;* the second is *dimethyl-ethyl-methane;* and the third *tetramethyl-methane.*

Proofs.—Normal pentane is obtained by replacing the group CN of the cyanide of normal butane by hydrogen. We have seen above how the formula of the cyanide itself is determined.

Dimethyl-ethyl methane is derived from ordinary amyl alcohol, and hence has the same general constitution. The proofs for the constitution of this alcohol will be given below.

Tetramethyl-methane is derived from the iodide of tertiary butyl alcohol by the action of zinc methyl. The reaction is believed to take place as follows:

$$2\,CH_3.CI(CH_3)_2 + Zn(CH_3)_2 = 2\,C(CH_3)_4 + ZnI_2$$

Iodide of tertiary butyl alcohol. Tetramethyl-methane.

A great variety of substitution products can be obtained from the isomeric butanes. Of the alcohols theory indicates the possible existence of eight, of which seven are known. These are:

1. Normal amyl alcohol (butyl carbinol),

$$CH_3.CH_2.CH_2.CH_2.CH_2OH.$$

2. Isoamyl alcohol (methyl-propyl carbinol),

$$CH_3.CH_2.CH_2.CHOH.CH_3.$$

3. Diethyl carbinol,

$$CH_3.CH_2.CHOH.CH_2.CH_3.$$

4. Inactive amyl alcohol (isobutyl carbinol),

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!\rangle CH.CH_2.CH_2OH.$$

5. Active amyl alcohol (secondary butyl carbinol),

$$CH_3.CH_2.CH\langle\begin{matrix} CH_3 \\ CH_2OH \end{matrix}.$$

6. Methyl-isopropyl carbinol,

$$CH_3.CHOH.CH\langle\begin{matrix} CH_3 \\ CH_3 \end{matrix}.$$

7. Dimethyl-ethyl carbinol,

$$CH_3.CH_2.COH\langle\begin{matrix} CH_3 \\ CH_3 \end{matrix}.$$

These alcohols, like the others which have been considered, form the starting-points for the preparation of corresponding substitution products.

Proofs.—Normal amyl alcohol is obtained from normal valeric acid, and yields this acid by oxidation. The constitution of the acid follows from its method of preparation. (See Normal Valeric Acid.)

Methyl-propyl carbinol yields methyl-propyl ketone, $CH_3—CO—C_3H_7$, by oxidation, and is formed by reduction of this compound.

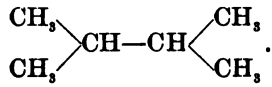
Diethyl carbinol yields diethyl ketone, $C_2H_5—CO—C_2H_5$, by oxidation.

Isobutyl carbinol yields by oxidation an acid which has been shown to have the formula $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH.CH_2.COOH$.

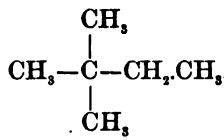
Secondary Butyl Carbinol.—For reasons which will be considered further on, it has been suggested that in bodies which are optically active, there is a carbon atom linked to four different kinds of atoms or groups. Such an atom is called *asymmetrical.* Now, as secondary butyl alcohol is an optically active body, it is believed to contain an asymmetrical carbon atom. Further, it is a primary alcohol, and hence probably contains the group CH_2OH. The only formula which is in accordance with these facts is

$$CH_2OH—\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}—C_2H_5,$$
$$\quad\quad\quad

4. Di-isopropyl (Tetramethyl ethane),



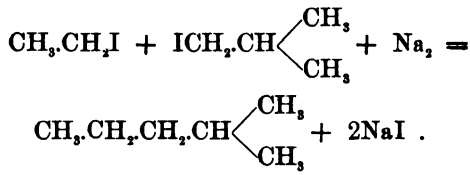
5. Trimethyl-ethyl methane,



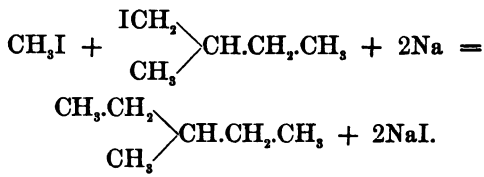
Proofs.—Normal hexane is formed when normal propyl iodide is heated with sodium:

$$H_3C.CH_2.CH_2I + ICH_2.CH_2.CH_3 + Na_2 = CH_3.CH_2.CH_2.CH_2.CH_2.CH_3 + 2NaI.$$

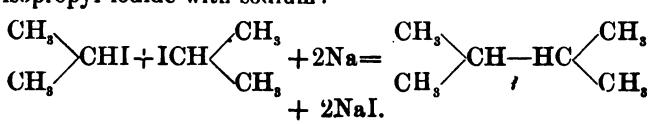
Dimethyl-propyl methane is formed from ethyl iodide and isobutyl iodide by treating the mixture with sodium:



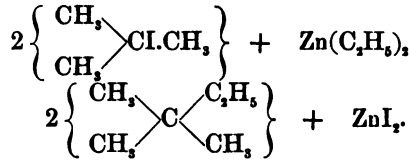
Methyl-diethyl methane is formed by treating a mixture of methyl iodide and active amyl iodide with sodium:



Di-isopropyl (tetramethyl ethane) is formed by treating isopropyl iodide with sodium:

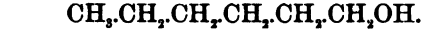


Trimethyl-ethyl methane is obtained by the action of zinc ethyl on tertiary butyl iodide:

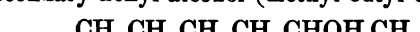


Eight alcohols are known which are derived from the hexanes. They are:

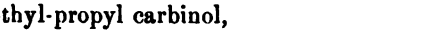
1. Primary hexyl alcohol,



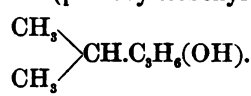
2. Secondary hexyl alcohol (methyl-butyl carbinol),



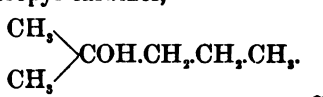
3. Ethyl-propyl carbinol,

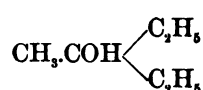


4. Caproyl alcohol (primary isohexyl alcohol),

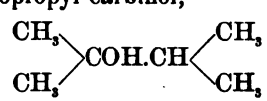


5. Dimethyl-propyl carbinol,

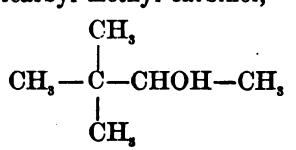


6. Methyl-diethyl carbinol,  .

7. Dimethyl-isopropyl carbinol,

 .

8. Trimethylcarbyl-methyl carbinol,

 .

Proofs.—The proofs of the constitution of the hexyl alcohols are very similar to those considered under the head of the amyl alcohols.

Derivatives of Heptane, C_7H_{16}. — Of the nine hydrocarbons of the formula C_7H_{16}, the existence of which is indicated by the theory, only four are known up to the present:

1. Normal heptane, $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_3$.

2. Isoheptane (dimethyl-butyl methane),

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH.CH_2.CH_2.CH_2.CH_3.$$

3. Triethyl methane, $CH_3.CH_2-\underset{\displaystyle CH_2.CH_3}{\overset{\displaystyle CH_2.CH_3}{\overset{|}{\underset{|}{CH}}}}$.

4. Dimethyl-diethyl methane, $CH_3-\underset{\displaystyle CH_2.CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2.CH_3$.

A large number of alcohols have been prepared, and the connection between them and the heptanes established. It is unnecessary to consider them here.

Monobasic Acids, $C_nH_{2n}O_2$.

The acids of this series may be considered as substitution products of the hydrocarbons, formed by replacing a hydrogen atom of the latter by carboxyl (COOH). In most cases these acids have been prepared by converting the group CN of the cyanides of hydrocarbon residues into COOH. If we know the constitution of the cyanide, the constitution of the acid is readily deduced.

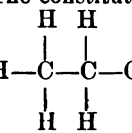
The principal members of the series are:

Formic acid,	H.COOH.
Acetic acid,	CH_3.COOH.
Propionic acid,	C_2H_5.COOH.
Butyric acid,	C_3H_7.COOH.
Valeric acid,	C_4H_9.COOH.
Caproic acid,	C_5H_{11}.COOH.

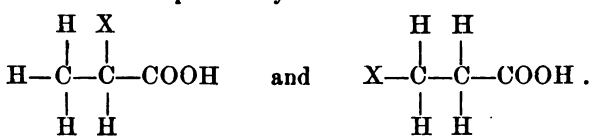
Of formic acid and its substitution products only one variety is known.

Of acetic acid and its substitution products, also, only one variety is known.

Propionic Acid.—With propionic acid the case is different. Of the acid itself only one variety is known, but of the mono-substitution products two varieties are known. The constitution of the acid is represented thus:



Now it is plain that, in this compound, aside from the hydrogen of the carboxyl group, there are two kinds of hydrogen atoms—those combined with a carbon atom which in its turn is in combination with the group CH_2, and those in combination with a carbon atom which in its turn is in combination with two carbon atoms. The case is similar to that of propane, of which we saw that two varieties of substitution products are possible. The two possibilities are expressed by the formulas:



Those which have the first formula are called α-substitution products; those which have the second are called β-substitution products. The best known representatives of these two classes are two lactic acids. The lactic acids are derived from proprionic acid by substituting hydroxyl for a hydrogen atom. β-iodo-propionic acid is converted into hydracrylic acid (one of the lactic acids) when boiled with water.

The change consists in substituting hydroxyl (OH) for the iodine. Hydracrylic acid is formed from ethylene, which will be shown to have the formula $\begin{matrix}CH_2\\|\\CH_2\end{matrix}$, by the following reactions:

Ethylene takes up hypochlorous acid, HClO, and becomes $\begin{matrix}CH_2OH\\|\\CH_2Cl\end{matrix}$, ethylene-chlorhydrin This product is easily transformed into ethylene-cyanhydrin, $\begin{matrix}CH_2OH\\|\\CH_2.CN\end{matrix}$, and this in turn into hydracrylic acid, $\begin{matrix}CH_2OH\\|\\CH_2.COOH\end{matrix}$.

The constitution of hydracrylic acid is easily deduced from these reactions. As β-iodo-propionic acid is converted into hydracrylic acid by boiling water, it further follows that β-iodo-propionic acid has the constitution

$$\begin{matrix}CH_2I\\|\\CH_2COOH\end{matrix} \quad \text{or} \quad \begin{matrix}H\ \ H\\|\ \ |\\I—C—C—COOH\\|\ \ |\\H\ \ H\end{matrix} .$$

All mono-substitution products of propionic acid which have been converted into or formed by simple reactions from β-iodo-propionic acid are called β-compounds, and they are all assumed to have the same general constitution.

Having determined the constitution of the β-compounds, that of the α-compounds follows. It must be represented by the other possible formula.

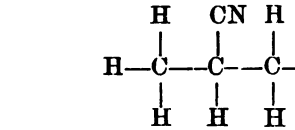
Butyric Acids.—Two acids of the formula $C_3H_7.COOH$ are theoretically possible, and two are known. These are *normal butyric acid*, $CH_3.CH_2.CH_2.COOH$, and *isobutyric acid*, $\begin{matrix}CH_3\\\\CH_3\end{matrix}\!\!>\!CH.COOH$.

Proofs.—Normal butyric acid is prepared by introducing the group C_2H_5 into acetic acid, by a reaction the essential part of which is represented by the equation:

$$CH_2Na.COOH + C_2H_5I = C_2H_5.CH_2.COOH + NaI.$$

Further, by reduction, normal butyric acid yields one of the two possible primary butyl alcohols. It was shown (p. 177) that the other possible primary butyl alcohol is not a derivative of normal butane; consequently normal butyric acid must have a constitution like that of normal butane, and it has the formula above assigned to it.

Isobutyric acid is obtained from isopropyl cyanide (p. 175), and this has been shown to have the constitution



From this the above formula follows for isobutyric acid.

Valeric Acids.—Four acids of the formula $C_5H_{10}O_2$ are known. These are:

1. Normal valeric acid, $CH_3.CH_2.CH_2.CH_2.CO.OH$.
2. Inactive valeric acid, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH.CH_2.COOH$.
3. Active valeric acid, $CH_3.CH\!<\!\begin{matrix}CH_2.COOH\\CH_3\end{matrix}$.
4. Trimethylacetic acid, $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-COOH$.

Proofs.—*Normal valeric acid* may be prepared indirectly from normal butyl alcohol by three reactions:

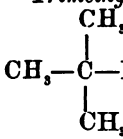
$$CH_3.CH_2.CH_2.CH_2OH+HCl=CH_3.CH_2.CH_2.CH_2Cl+H_2O.$$

$$CH_3.CH_2.CH_2.CH_2Cl + KCN = CH_3.CH_2.CH_2.CH_2CN + KCl.$$

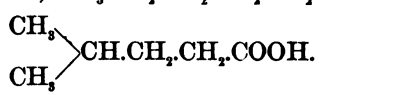
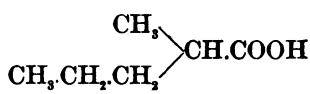
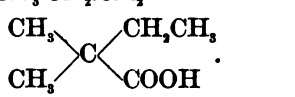
$$CH_3.CH_2.CH_2.CH_2CN+2H_2O=CH_3.CH_2.CH_2.CH_2.COOH+NH_3.$$

Inactive valeric acid is formed from isobutyl iodide, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH.CH_2I$, by making the cyanide and converting the cyanogen group into carboxyl.

Active valeric acid is formed by oxidizing active amyl alcohol (secondary butyl alcohol).

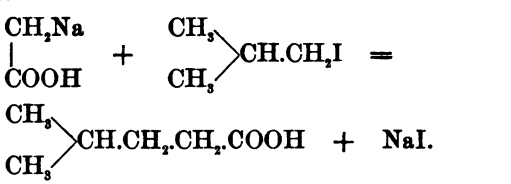
Trimethylacetic acid is made from tertiary butyl iodide  , through the cyanide.

Caproic Acids.—Five acids of the formula $C_6H_{12}O_2$ are known. These are:

1. Normal caproic acid, $CH_3.CH_2.CH_2.CH_2.CH_2.COOH$.
2. Isocaproic acid, 
3. Diethylacetic acid,
4. Methylpropylacetic acid, 
5. Dimethylethylacetic acid,  .

Proofs.—Normal caproic acid is obtained by oxidation of normal hexyl alcohol, and from normal amyl iodide through the cyanide.

Isocaproic acid has been prepared by introducing isobutyl into acetic acid:



Diethylacetic acid is obtained by introducing two ethyl groups into acetic acid:

$$\begin{matrix}CHNa_2\\|\\COOH\end{matrix} + 2C_2H_5I = \begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>\!CH.CO.OH + 2NaI.$$

Dimethylethylacetic acid is prepared indirectly from dimethylethyl carbinol, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C\!<\!\begin{matrix}C_2H_5\\OH\end{matrix}$, by introducing iodine in the place of hydroxyl, then substituting the cyanogen group for the iodine and converting the cyanogen into carboxyl.

The other acids of this series are not very well known. By the aid of the foregoing examples, the method of determining the constitution of the known acids will be readily understood.

Aldehydes.—Corresponding to every primary alcohol and to every acid an aldehyde is possible. The constitution of each of these aldehydes is given if we know from which acid or from which alcohol it is obtained.

The aldehydes are produced from the primary alcohols by partial oxidation; and from the acids by subjecting a mixture of a salt of the acid and a salt of formic acid to dry distillation.

Acetones or Ketones.—The ketones are obtained by distilling mixtures of two acids. If the constitution of the acid is known, that of the ketone obtained in each case is also known.

Diacid Alcohols, $C_nH_{2n+2}O_2$.—The alcohols thus far considered are the simplest. They act like mon-acid bases, as KOH, NaOH, etc. Corresponding to diacid bases there are also diacid alcohols. The simplest substance of this kind known is *ethylene alcohol* or *glycol*, $C_2H_6O_2$. When this substance is carefully examined, it is found to act like an alcohol, and not in any respect like acids, aldehydes, ketones, etc. Between it and ordinary alcohol there is, however, one marked difference. The reactions characteristic of ordinary alcohol can be carried further with this substance. Thus, while from the former only one metallic deriv-

ative, C_2H_5OK, can be obtained with any one metal, from ethylene alcohol two such derivatives can be obtained, viz.: $C_2H_5O_2K$ and $C_2H_4O_2K_2$. One hydrogen and all the oxygen of ordinary alcohol are replaced by chlorine under the influence of the chlorides of phosphorus, the product C_2H_5Cl being formed; while, according to the quantity of the chloride of phosphorus brought into action, two different chlorides may be obtained from ethylene alcohol, viz.: C_2H_5OCl and $C_2H_4Cl_2$. By oxidation ordinary alcohol yields but one acid, and that is monobasic. By oxidation two different acids may be obtained. One of these, of the formula $C_2H_4O_3$, is monobasic, and has the peculiarity that it combines in itself the properties of an acid and an alcohol; the other, of the formula $C_2H_2O_4$, is bibasic.

These facts can best be explained by assuming that in ethylene alcohol there are two hydroxyls, or, in other words, that the characteristic grouping of the hydrogen and oxygen in ordinary alcohol is twice repeated in ethylene alcohol.

This conception of the nature of ethylene alcohol finds expression in the formula $C_2H_4\begin{matrix}OH\\OH\end{matrix}$.

This formula has been verified by a synthesis, the principle of which is represented in the equation:

$$C_2H_4Br_2 + 2Ag(OH) = C_2H_4\begin{matrix}OH\\OH\end{matrix} + 2AgBr.$$

Accepting the formula, the reactions referred to may be interpreted thus:

$$C_2H_4\begin{matrix}OH\\OH\end{matrix} + K = C_2H_4\begin{matrix}OK\\OH\end{matrix} + H;$$

$$C_2H_4\begin{matrix}OK\\OH\end{matrix} + K = C_2H_4\begin{matrix}OK\\OK\end{matrix} + H;$$

$C_2H_4\begin{matrix}OH\\OH\end{matrix}$ gives $C_2H_4\begin{matrix}Cl\\OH\end{matrix}$ and $C_2H_4\begin{matrix}Cl\\Cl\end{matrix}$;

$C_2H_4\begin{matrix}OH\\OH\end{matrix}$ gives $\begin{matrix}COOH\\|\\CH_2OH\end{matrix}$ and $\begin{matrix}COOH\\|\\COOH\end{matrix}$.

Hydroxy-acetic or glycolic acid. Oxalic acid.

Considering the oxidation products, and recalling what has already been said concerning the transformation of alcohols into acids, we are led to the belief that in ethylene alcohol there are two primary alcohol groups, CH_2OH, and that each of these in turn may be converted into carboxyl. In the light of these considerations, the formula $\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}$ for ethylene alcohol becomes extremely probable.

Monohydroxy Monobasic Acids, $C_nH_{2n}O_3$.—The simple fatty acids already considered, have the general formula $C_nH_{2n}O_2$. There is a series of monobasic acids, closely related to these, which have the formula $C_nH_{2n}O_3$. The simplest of these is identical with the first product of oxidation of ethylene alcohol. It is known as *glycolic* or *hydroxy-acetic acid*, and has the formula $C_2H_4O_3$. It is found to have the properties of an alcohol as well as an acid. The formula $\begin{matrix}CH_2OH\\|\\COOH\end{matrix}$ is in accordance with the facts. The presence of the alcoholic hydroxyl is inferred in the same way as in the case of simple alcohols. The formula suggests the possibility of converting the compound into a bibasic acid of the formula $\begin{matrix}COOH\\|\\COOH\end{matrix}$, a transformation which, as we have seen, may actually be effected.

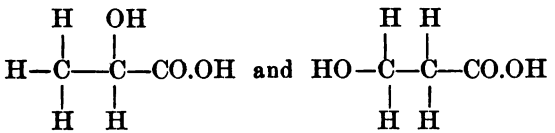
The synthesis of the acid furnishes further proof of the correctness of the view expressed by the formula. It has been prepared by treating chlor- or bromacetic acid with silver hydroxide:

$$\underset{\text{Bromacetic acid.}}{\begin{matrix}CH_2Br\\|\\COOH\end{matrix}} + AgOH = \underset{\text{Glycolic acid.}}{\begin{matrix}CH_2OH\\|\\COOH\end{matrix}} + AgBr.$$

All acids which, like glycolic acid, may be regarded as simple acids in which hydroxyl takes the place of hydrogen, are known as *hydroxy-acids*.

Hydroxypropionic Acids, $C_2H_4\begin{matrix}OH\\\diagdown\\COOH\end{matrix}$.—These acids are monohydroxyl derivatives of propionic acid. It has been

pointed out that of the mono-substitution products of propionic acid there are two varieties, known as the α- and β-compounds. Accordingly, we would expect the existence of two hydroxy-propionic acids of the formulas:



These are the only ones the existence of which is foretold by the theory. Nevertheless, no less than four compounds have been described as hydroxy-propionic acids. These are:

1. *α Hydroxy-propionic acid*, or inactive ethylidene lactic acid. This is ordinary lactic acid, obtained by fermentation of milk.
2. *Paralactic acid*, or sarcolactic acid, also called ethylidenelactic acid.
3. *Ethylenelactic acid*, and
4. *Hydracrylic acid.*

As there seems to be some doubt regarding the existence of the third acid, ethylenelactic acid, it need not be discussed here.

α-Hydroxy-propionic acid is obtained by substituting hydroxyl for chlorine in α-chlorpropionic acid. It is also made from the compound $CH_3.CH\langle^{Cl}_{Cl}$ (obtained from aldehyde by treatment with phosphorus pentachloride) by substituting hydroxyl for one and carboxyl for the other chlorine. It is optically inactive, that is, it has no perceptible effect on polarized light.

Paralactic acid acts towards reagents like ordinary lactic acid, and is hence shown to belong to the α series. Unlike the ordinary acid, however, it exerts a decided influence on polarized light.

The isomerism of these two acids cannot be explained by our ordinary formulas. It is possible that a suggestion made by Le Bel and afterwards by van't Hoff, may furnish the true explanation. This suggestion has reference to a possible new kind of isomerism in the case of optically active substances. It will be briefly taken up in the last section. Atten-

tion may be directed here to the fact that ethylidenelactic acid contains what has been called (see p. 180) an *asymmetrical carbon atom*, $H_3C-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-COOH$. It is upon this fact that the explanation of the peculiar isomerism is based.

Hydracrylic acid is made from β-iodo-propionic acid, and is hence a β-compound. It is also made from ethylene by adding hypochlorous acid and substituting carboxyl for the chlorine in the resulting compound, as has been explained (see p. 185).

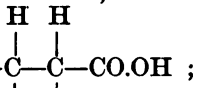
Bibasic Acids, $C_nH_{2n-2}O_4$. — *Oxalic acid*, $C_2H_2O_4$, or $\begin{matrix}COOH\\|\\COOH\end{matrix}$, is the simplest representative of these acids possible. It is bibasic, and the same reactions by which we are led to conclude that carboxyl, COOH, is present in the monobasic acids leads us, also, to conclude that, in the bibasic acids, there are two carboxyls present.

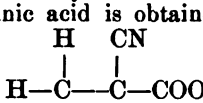
The second member of this series is *malonic acid*, $CH_2\begin{matrix}COOH\\COOH\end{matrix}$. Of each of these acids only one variety is possible.

The third member is *succinic acid*, $C_2H_4\begin{matrix}COOH\\COOH\end{matrix}$. Of this there should be two varieties corresponding to the two lactic acids, or the two series of mono-substitution products of propionic acid. For succinic acid may plainly be considered as propionic acid in which a hydrogen atom has been replaced by a carboxyl group. The two succinic acids should have the following formulas:

1. $H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{CO.OH}{|}}{\underset{\underset{H}{|}}{C}}-CO.OH$ and 2. $CO.OH-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-CO.OH$

The second formula is that of ordinary *succinic acid*, and the first that of *isosuccinic acid.*

Proofs.—Ordinary succinic acid is obtained from β-cyanpropionic acid, the constitution of which we know to be  ; and from ethylene cyanide. , which is obtained by treating ethylene bromide with potassium cyanide.

Isosuccinic acid is obtained from α-cyanpropionic acid, which is  .

Triacid Alcohols and Tribasic Acids.

Glycerin.—Only one alcohol is well known which contains three hydroxyl groups. This is glycerin. Such alcohols are known as triacid alcohols. The formula of glycerin is . This formula is very probable, because, as a result of a large number of observations on carbon compounds, it seems to be a general truth that one carbon atom cannot, except under peculiar conditions, hold in combination more than one hydroxyl group. If this be true, the above formula is the only one possible for glycerin. But, again, by oxidation, glycerin yields a monobasic acid containing the same number of carbon atoms; and, by further oxidation, apparently a bibasic acid also containing the same number of carbon atoms. These facts would show that the group CH_2OH occurs twice in glycerin. But if there are

two groups CH_2OH present in glycerin, then the formula above accepted must be correct.

Glyceric Acid is obtained by partially oxidizing glycerin. As the acid contains the same number of carbon atoms as glycerin contains, it is assumed that the oxidation consists in a transformation of the primary alcohol group CH_2OH into COOH; hence, the formula of glyceric acid is $\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ COOH \end{matrix}$. According to this, a bibasic acid, $\begin{matrix} COOH \\ | \\ CHOH \\ | \\ COOH \end{matrix}$, ought to be obtained by oxidizing glyceric acid, just as this bibasic acid is obtained by oxidizing glycerin. This transformation has not yet been effected.

More Complex Alcohols and Acids.

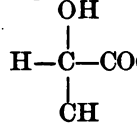
Among the best known substances of greater complexity analogous to those thus far considered are *tartaric acid* and *citric acid*. The former is a bibasic acid, containing, in addition to the two carboxyl groups, two alcoholic hydroxyl groups. It is hence a bibasic tetratomic acid. It is dioxysuccinic acid, and must have the formula $\begin{matrix} CH.OH.COOH \\ | \\ CH.OH.COOH \end{matrix}$. It is obtained from dibromsuccinic acid by treating the latter with water, thus:

$$\begin{matrix} CHBr.COOH \\ | \\ CHBr.COOH \end{matrix} + 2H_2O = \begin{matrix} CH.OH.COOH \\ | \\ CH.OH.COOH \end{matrix} + 2HBr.$$

Dibromsuccinic acid. Tartaric acid.

As in the case of the hydroxy-propionic acids, there are substances isomeric with tartaric acid, for which the commonly accepted theories of constitution do not account. It is possible that we have here to deal with conditions of

structure similar to those met with in connection with the hydroxy-propionic acids. Tartaric acid, like *a*-hydroxy-propionic acid, contains an *asymmetrical carbon atom*,



Citric acid is tribasic, containing, in addition to its three carboxyl groups, one alcoholic hydroxyl. These facts are represented in the formula $C_3H_4(OH)\begin{cases}COOH\\COOH\\COOH\end{cases}$.

In addition to the compounds considered, there are others still more complex, and derived from the marsh-gas hydrocarbons by the substitution of five and six alcoholic hydroxyls, etc., for hydrogen. Of those containing five hydroxyls, there is only one representative known. Of those containing six substituting groups, however, a large number is known. Among these are the different varieties of sugars, cellulose, and starch; and the acids which are derived from them. All that is positively known of these compounds is that they contain a certain number of hydroxyl groups, or of hydroxyl and carboxyl groups. The presence of the carboxyl groups is detected through the acid properties of the substance. If the substance is a monobasic acid, one carboxyl group is assumed to be present in it; if it is a bibasic acid, two carboxyl groups are assumed to be present in it, etc. The number of hydroxyl groups present is determined by allowing acetyl chloride or acetic anhydride to act upon the compound. If the latter contains only one hydroxyl, it will take up only one acetyl group, C_2H_3O; if it contains two hydroxyl groups, it will take up two acetyl groups, etc.

An examination of the alcohols referred to in the preceding pages reveals the fact that the simplest mon-acid alcohol, CH_4O, contains only one carbon atom; the simplest di-acid alcohol, $C_2H_6O_2$, contains two; the simplest tri-acid alcohol, $C_3H_8O_3$, contains three; the simplest tetracid alcohol, $C_4H_{10}O_4$, contains four; and the simplest hex-acid alcohol contains six. This is another illustration of the

truth that, except under peculiar conditions, one carbon atom can hold in combination but one hydroxyl.

Cyanogen Compounds.

In speaking of the group CN, under the head of substitution, it was shown that in the cyanides the arrangement is probably R—C—N (see p. 144). Cyanogen itself is commonly represented by the formula

$$\begin{array}{l} C{-}N \\ | \\ C{-}N \end{array} \quad \text{or} \quad \begin{array}{l} C{\equiv}N \\ | \\ C{\equiv}N \end{array} .$$

The simplest compound of cyanogen is hydrocyanic acid, which probably consists of the group —C—N united with hydrogen, viz.: H—C—N (or H—C≡N(?)).

The hydrogen atom of this acid may be replaced by a variety of groups or other elements, as, for instance, OH, SH, NH_2, etc. Thus, a large number of derivatives are obtained which have a constitution similar to that of the acid. Thus we have *cyanic acid*, HO—C—N; *sulphocyanic acid*, HS—C—N; *cyanamide*, H_2N—C—N, etc.

It has already been shown that there are compounds containing the group C—N— (or C≡N—) called carbamines, which are isomeric with the hydrocarbon cyanides, and the proofs for the formula C—N— have also been given (see *ante*, p. 145).

Mustard Oils. — Sulphocyanic acid, HS—C—N, like other acids, yields salts and ethers by exchanging its hydrogen for metals or hydrocarbon residues. We have potassium sulphocyanate, KS—C—N; methyl sulphocyanate, CH_3—S—C—N, etc. Running parallel to the ethers of sulphocyanic acid is a series of compounds known as mustard oils. These have the same composition as the above ethers, but entirely different properties and constitution.

The simplest representative of this series is *methyl mustard oil*, which has the constitution expressed by the formula S—C—N—CH_3. A number of corresponding compounds are known, one of which is *allyl mustard oil*, S—C—N—C_3H_5. This is the oil obtained from black mustard seed.

The proofs of the constitution assigned to the mustard oils are as follows:

Ethyl mustard oil is formed by a somewhat circuitous method. When carbon bisulphide, CS_2, is brought in contact with ethylamine, $N\begin{cases}C_2H_5\\H\\H\end{cases}$, the ethylamine salt of ethylsulphocarbamic acid is formed, thus:

$$CS_2 + 2(NH_2.C_2H_5) = CS\begin{cases}NH.C_2H_5\\SH.NH_2.C_2H_5\end{cases}.$$

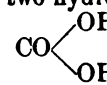
By appropriate reactions this salt is split up into ethylamine, hydrogen sulphide, and ethyl mustard oil. The decomposition can be best interpreted as follows:

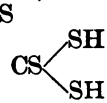
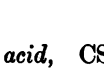
$$CS\begin{cases}N\,H\,|\,.\,C_2H_5\\S\,H\,|\,.\,NH_2.C_2H_5\end{cases}.$$

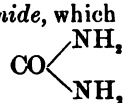
Hence the resulting mustard oil apparently retains an atom of sulphur united with carbon alone, and the carbon in turn is probably also united directly with the residue of ethylamine, $—N.C_2H_5$. If we examine the products of decomposition of ethyl mustard oil, we are also led to the formula above given. With water or hydrochloric acid it yields ethylamine, carbon dioxide, and hydrogen sulphide; with nascent hydrogen it yields ethylamine, formic thioaldehyde, and hydrogen sulphide. The production of ethylamine indicates clearly that in the mustard oil, the ethyl group is in combination with the nitrogen atom; and the production of formic thioaldehyde, which differs from formic aldehyde, H.COH, only in containing sulphur in the place of oxygen, also indicates that in ethyl mustard oil the sulphur atom is in combination with carbon. These results are embodied in the formula accepted for the mustard oil.

The ether of sulphocyanic acid, which is isomeric with ethyl mustard oil, conducts itself towards reagents in an entirely different manner. It never yields ethylamine, but always a compound in which the ethyl group is in combination with sulphur, as ethyl sulphide or ethyl sulphurous acid; while the nitrogen is split off in combination with hydrogen alone, or with carbon, hydrogen, and oxygen.

Derivatives of Carbonic Acid.

The salts of carbonic acid have the general formula M_2CO_3. They are derived from a bibasic acid, H_2CO_3. This acid being bibasic probably contains two hydroxyl groups, and hence we are led to the formula  for carbonic acid. No such acid is known. If we attempt to prepare it from its salts, we always get the compound CO_2, which may justly be considered as the anhydride of the true carbonic acid. It has already been stated, that it appears to be a law, that one carbon atom cannot hold in combination more than one hydroxyl group. This breaking up of carbonic acid into water and the anhydride is an indication of the truth of the law. Whether the acid is formed or not when the anhydride is conducted into water, is not yet decided.

Though we are not acquainted with carbonic acid, we are acquainted with a very large number of its derivatives. These are obtained, 1, by replacing the hydrogen of the acid by elements or groups; 2, by replacing one or both of the hydroxyl groups by groups or elements; 3, by replacing the oxygen by sulphur. Thus we obtain first a series of salts and ethers; then compounds, such as *carbonyl chloride*, , *carbon sulphoxide*, , carbon bisulphide, ; and finally such compounds as *sulphocarbonic acid*,  , *xanthogenic acid*,  , etc.

Among the most important derivatives of carbonic acid is the amide *urea* or *carbamide*, which has the constitution expressed by the formula  .

The proofs of this formula are as follows:

It is formed by the action of carbonyl chloride upon ammonia, thus:

$$COCl_2 + 2NH_3 = CO\begin{matrix}NH_2\\NH_2\end{matrix} + 2HCl\ .$$

Also by the action of ammonia upon ethylcarbonate, thus:

$$CO\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix} + 2NH_3 = CO\begin{matrix}NH_2\\NH_2\end{matrix} + 2(C_2H_6O)\ .$$

The latter is a general reaction employed for the production of acid amides from the ethers.

Urea has the power of uniting with bases, acids, and salts, and of forming with them crystallized compounds. Instead of the ammonia residue NH_2 it may contain residues of the amine bases, as $NH.CH_3$, $NH.C_2H_5$, etc. Or, again, one or more of the hydrogen atoms of urea may be replaced by acid residues, such as C_2H_3O, C_7H_5O, etc.

A large number of compounds are allied to and derived from *uric acid*. They have frequently been the subjects of exhaustive investigations, but up to the present no formula has been proposed for uric acid which is in every respect satisfactory. It is a weak bibasic acid, but it does not contain two carboxyl groups, for its formula is $C_5N_4H_4O_3$, while a compound which contains two carboxyl groups must contain four atoms of oxygen. The presence of the group —C—N seems to be pretty clearly indicated in the acid, for it yields, with great ease, products which certainly contain this group. The amide group NH_2 is also probably present in it, for, when heated with hydriodic acid, it yields, among other products, glycocol or amido-acetic acid,

$$CH_2\begin{matrix}NH_2\\COOH\end{matrix}\ .$$

Unsaturated Compounds Allied to the Marsh-Gas Derivatives.

The hydrocarbons and their derivatives which have thus far been considered, have the peculiarity in common, that nothing can be added directly to them. In order to change them something must first be removed from them. When treated with strong reagents, the first kind of action which takes place is substitution. Thus marsh-gas, CH_4, and chlorine yield CH_3Cl, CH_2Cl_2, etc., and not CH_4Cl, CH_4Cl_2. Compounds which act in this way are called *saturated compounds.* The condition of saturation is undoubtedly dependent upon the property of valence, and, in the terms of the valence hypothesis, it is explained by saying that in the saturated compounds all the bonds or affinities of the elements are satisfied.

There remain a large number of carbon compounds which do not act in the manner described. When treated with strong reagents, such as chlorine, bromine, etc., these elements are taken up directly. In many cases substitution does not take place until a definite quantity of the elements has been added. Addition is the first kind of action. Thus, the hydrocarbon ethylene, C_2H_4, when treated with bromine, yields the addition-product $C_2H_4Br_2$:

$$C_2H_4 + Br_2 = C_2H_4Br_2 .$$

If the bromine be present in larger quantity than is necessary to complete this reaction, substitution takes place as in the case of saturated compounds:

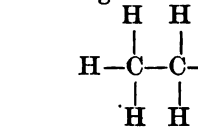
$$C_2H_4Br_2 + Br_2 = C_2H_3Br_3 + HBr, \text{ etc.}$$

Ethylene is the representative of quite a large class of compounds in regard to which the general statement may be made that *they have the power of taking up directly two atoms of bromine, chlorine, etc., or one molecule of hydrochloric, hydrobromic, or hydriodic acid.* The products formed act like saturated compounds, and may indeed, in most cases, be shown to be intimately connected and frequently identical with the products obtained by substitution from the marsh-gas hydrocarbons and their derivatives.

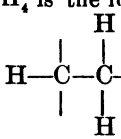
What difference is there then in the constitution of the marsh-gas derivatives proper, and the unsaturated com-

pounds which are analogous to ethylene? Or, to simplify the discussion, what is the difference between ethane, C_2H_6, and ethylene, C_2H_4?

All that we know is that the former cannot take up directly bromine, chlorine, hydrobromic acid, etc., while the latter can take up a definite quantity of these substances. Assuming that in ethane the carbon atoms are linked together as commonly represented, we have the formula:

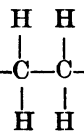


. The simplest change that we can conceive of that would give the compound C_2H_4 is the loss of two of the hydrogens, giving either



,

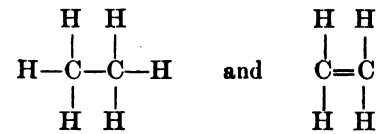
or



. In both cases, unless we suppose something besides the simple loss of hydrogen to have taken place, there are left what are called "free bonds." The expression is contradictory, and may be replaced with advantage by "free affinities." The conception of free affinities is purely hypothetical. We know nothing whatever about the condition existing between the carbon atoms in unsaturated compounds, any more than we do about the conditions between the carbon atoms in saturated compounds. Without entering fully into the discussion regarding the theory of unsaturated compounds,* it need only be stated here that two views have prevailed. According to one, there are actually free affinities in the compounds as represented in the formulas above given for ethylene. According to the other, the carbon atoms in unsaturated compounds bear a different relation to each other from that which exists in saturated compounds. The character of this difference is supposed to

* For a full and instructive discussion of this subject, see particularly, Lossen, Annalen der Chemie, Vol. 204, p. 265.

be expressed by the formulas C—C and C=C, or, in the case of the two hydrocarbons ethane and ethylene, by



This suggestion is plainly the result of a rigid application of the valence hypothesis. It starts with the assumption that the carbon atom must have four affinities or bonds, and that these must be used in some way. Now, if there is not hydrogen enough to satisfy these affinities, the unused affinities of the carbon atoms act upon each other, giving what is known as *double linkage* or double union. According to this idea it would appear at first sight at least that carbon atoms, which are doubly linked, ought to be more firmly held together than those which are singly linked. The opposite appears, however, to be true. Saturated compounds appear to be particularly liable to decomposition at the places where the double linkage is supposed to exist.

On the other hand, a serious objection to the "free affinity" hypothesis is that it involves the idea of a part of an atom being employed while another part is unemployed; and, whatever view we may hold regarding the nature of atoms, this kind of division appears absurd.

It seems much more probable that in the unsaturated hydrocarbons the relations existing between all the constituents are different from those in the corresponding saturated compounds. As, however, we know nothing about the character of these differences, we cannot express them by formulas, and it is better not to commit ourselves to such a sign as the double line in C=C, as this appears to involve the definite view that the union between the carbon atoms is twice as strong, in the unsaturated condition, as it is in the saturated. It would be better to express this relation by some new sign, as, for instance, $\diamond$, to which no other meaning should be attached than that it represents the kind of union which exists between the carbon atoms in ethylene. Ethylene would then be represented by the formula $H_2C\diamond CH_2$. A body thus represented has the power of taking up bromine, chlorine, etc., in the same way as ethylene.

Ethylene and Derivatives.—In connection with ethane derivatives it was stated that two chlorides are known, both of which have the formula $C_2H_4Cl_2$. One of these is obtained from aldehyde by replacing the oxygen atom by two chlorine atoms; hence its formula was assumed to be $CHCl_2.CH_3$. The isomeric compound has the formula

$$\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array}.$$

This latter compound is obtained from ethylene by direct addition of chlorine, whence it is concluded that ethylene itself is symmetrical, *i. e.*, that each carbon atom in it holds in combination two hydrogen atoms, giving the constitution expressed by the formula $H_2C{<>}CH_2$.

Propylene, etc.—The remaining hydrocarbons of this series are obtained for the most part by treating the chlorides, bromides, or iodides of the hydrocarbons of the methane series with alcoholic potas-a, by which means ClH, BrH, or IH is abstracted from the compound. Thus, from C_3H_7I we obtain C_3H_6; from C_4H_9I we obtain C_4H_8, etc.

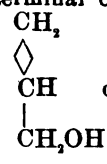
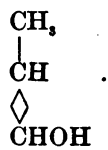
In many cases the method of formation of the hydrocarbon leads us directly to its constitution. In some cases a doubt exists even after all the methods of formation and the products of decomposition are taken into consideration.

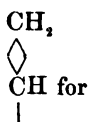
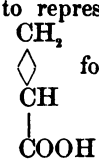
Alcohols.—Theoretically, a series of alcohols is possible, derived from the hydrocarbons of the ethylene series by the replacement of one hydrogen atom with one hydroxyl group. Only one such alcohol is known. This is allyl alcohol, $C_3H_5.OH$, or $CH_2{<>}CH.CH_2.OH$.

Proofs.—Allyl alcohol differs from propyl alcohol in containing two hydrogen atoms less. Now, by treating allyl alcohol with nascent hydrogen, it is converted into normal propyl alcohol, which, as we have seen, has the constitution

$$\begin{array}{l} \quad H\ \ H\ \ H \\ \quad |\ \ \ |\ \ \ | \\ H—C—C—C—OH \\ \quad |\ \ \ |\ \ \ | \\ \quad H\ \ H\ \ H \end{array}.$$

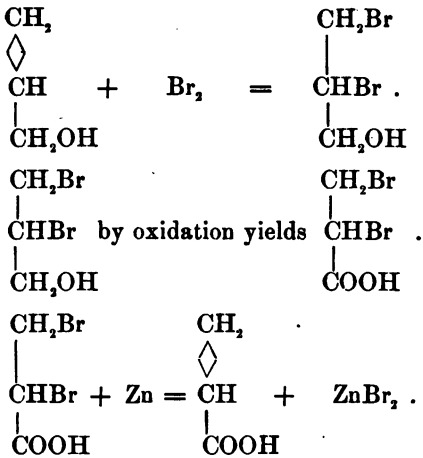
Hence it is assumed that in allyl alcohol, as well as in propyl alcohol, the hydroxyl is in

combination with one of the termiual carbon atoms, and, accordingly, it must be either  or  .

Acrylic acid, which is evidently closely related to allyl alcohol, is formed from β-iodo-propionic acid by the abstraction of hydriodic acid. β-iodo-propionic acid, further, is formed from acrylic acid by the addition of hydriodic acid. If the formula for β-iodo-propionic acid is correct, it follows that the formula  for acrylic acid is more probable than . Indeed, according to the valence hypothesis, the latter formula seems to represent an impossible compound. If the formula  for acrylic acid is correct, then the first of the two formulas above given for allyl alcohol is probably correct.

Acids.—Acrylic acid apparently bears the same relation to allyl alcohol that acetic acid bears to ordinary alcohol. Still, ordinary oxidizing agents do not convert the alcohol into the acid. This is probably due to the instability of the

unsaturated compound. Chromic acid converts allyl alcohol into the corresponding aldehyde, acroleïn, but continued action of the oxidizing agent causes the formation of formic acid. On the other hand, acroleïn may be converted into acrylic acid by means of a less active agent than chromic acid, as, for example, silver oxide. Further, if the alcohol be first converted into a saturated compound, by the addition of bromine, the resulting dibrompropyl alcohol conducts itself towards oxidizing agents the same as normal propyl alcohol. It yields a dibrompropionic acid, and this, when treated with zinc, loses bromine and yields acrylic acid. The reactions are:



From these changes we are led to the formula

for acrylic acid. This acid is the first of a series each member of which differs from the corresponding member of the series $C_nH_{2n}O_2$ by containing two hydrogen atoms less.

Acetylene. — By treating symmetrical bibromethane, $\begin{matrix}CH_2Br\\|\\CH_2Br\end{matrix}$, with an alcoholic solution of potassium hydroxide, hydrobromic acid is abstracted, and acetylene, a hydrocarbon of the formula C_2H_2, is formed:

$$C_2H_4Br_2 - 2HBr = C_2H_2.$$

This compound is a representative of a class of unsaturated compounds, differing from the ethylene derivatives in composition the same as the latter differ from the marsh-gas derivatives. The acetylene compounds have the power of taking up four atoms of chlorine or bromine or two molecules of hydrochloric or hydrobromic acid. Regarding the condition existing between the carbon atoms, a similar difference of views has prevailed to that noticed in connection with ethylene. The main question discussed has been whether in acetylene the presence of free affinities, or of triple linkage, is to be assumed, as represented in the formulas $\begin{matrix}H-C-C-H\\|\ \ |\\|\ \ |\end{matrix}$ and $H-C\equiv C-H$.

The remarks made about the two similar views regarding the structure of ethylene hold good here. It is better to adopt a new sign to represent the condition between the carbon atoms of acetylene and all similar compounds. In using it the only meaning to be attached to it is that it represents the kind of union which exists between the carbon atoms of acetylene. A convenient sign for the purpose is this $\diamond$, acetylene being represented thus: $HC\diamond HC$. The symmetrical distribution of the hydrogen atoms cannot, of course, be divined. It appears to follow, from the fact that acetylene is formed by abstracting hydrobromic acid from symmetrical bibromethane $\begin{matrix}CH_2Br\\|\\CH_2Br\end{matrix}$.

At least the simplest view of the reaction is represented thus:

$$\begin{matrix}CH|HBr\\|\ \ \ \ |\\CH|HBr\end{matrix} - 2HBr = \begin{matrix}CH\\|\\CH\end{matrix}.$$

Compounds Containing a Smaller Proportion of Hydrogen.—There are several hydrocarbons known which seem to be analogous in some respects to those already considered, but which differ from them in containing a smaller proportion of hydrogen. The principal of these are valylene, C_5H_8, and dipropargyl, C_6H_6. These take up bromine in larger quantity than the hydrocarbons, which contain more hydrogen. Thus, valylene gives $C_5H_8Br_6$, and dipropargyl gives $C_6H_6Br_8$. The products, it will be noticed, belong to the saturated compounds, the former being a substitution product of pentane, C_5H_{12}, and the latter bearing a similar relation to hexane, C_6H_{14}. Not enough is known about these substances to warrant us in forming a definite opinion in regard to their structure. It seems probable, however, that they are similar to ethylene and acetylene. Valylene may be represented by the formula $CH_3—C—C\diamond CH$, and dipropargyl by

$$\begin{array}{c} \diamond \\ CH_2 \end{array}$$

$CH\diamond C—CH_2—CH_2—C\diamond CH$. The formulas should, however, be regarded as tentative.

Benzene Derivatives. (Aromatic Bodies.)

A large class of compounds exists, the members of which possess the property in common that, when decomposed in a number of ways, they yield benzene as one of the products. Benzene itself has the formula C_6H_6. Just as the members of this class of compounds yield benzene as a decomposition product, so, also, they may be built up from benzene by the introduction of a variety of groups or elements in the place of hydrogen. All these compounds bear a relation to benzene similar to that which the fatty bodies bear to marsh-gas. In studying the aromatic bodies, then, it is plainly our first duty to determine the constitution of benzene itself, as the constitution of the derivatives cannot be understood until this determination is made.

Constitution of Benzene.—Whatever view we may entertain regarding the structure of benzene, the following facts must be first accounted for:

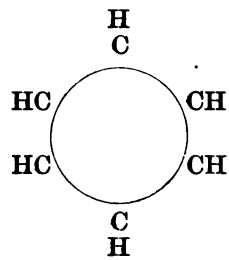
1. Of the substitution products of benzene which contain one substituting group, only one variety is known.

2. Of the substitution products of benzene which contain two substituting groups, three varieties have been observed, and only three.

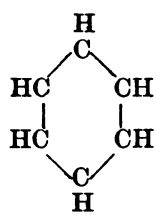
3. Of the substitution products of benzene which contain three substituting groups, more than three varieties have been observed.

A great deal of ingenious experimenting has been gone through with for the purpose of showing that the first of these statements is true. The method adopted may be briefly described. Starting with benzene, C_6H_6, one atom of hydrogen was replaced by bromine, a product, C_6H_5Br, being thus formed. Now a second hydrogen was replaced by some other group, say NO_2, the product $C_6H_4\begin{cases}Br\\NO_2\end{cases}$ being the result. It is plain that the NO_2 group must bear to the molecule a relation different from that which the bromine bears. Now the bromine was replaced by hydrogen, leaving the compound $C_6H_5(NO_2)$ with the group NO_2 presumably occupying the same position that it did in the compound $C_6H_4\begin{cases}Br\\NO_2\end{cases}$. Finally, the group NO_2 was replaced by bromine, and a compound, C_6H_5Br, was obtained in which the bromine replaced a different hydrogen atom from that replaced in the first compound. The two compounds were found to be identical, and the conclusion is drawn that two of the hydrogen atoms bear the same relation to the molecule. In a similar way the examination has been extended to all six of the hydrogen atoms, and the result reached is in accordance with the first general statement. It seems, hence, that all six hydrogen atoms in benzene bear the same relation to the molecule. We must, therefore, imagine the molecule of benzene to be symmetrically formed. Each one of the hydrogen atoms must be in combination with a single carbon atom, and what is true of one of them must be true of all the others. If we attempt to represent these ideas by a formula, it is plain that the formula must differ in some way from all those with which we have thus far had to deal. No one of these, representing a molecule with more than two carbon atoms, is strictly symmetrical. They represent the atoms as arranged in chains open at both ends. The simplest way in which we can represent the symmetrical character of benzene is by means of a circle. We may suppose the six atoms of carbon arranged at equal distances in

a circle, and the six hydrogen atoms in combination with them, thus:

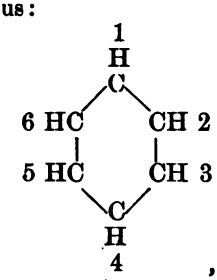


Of course the curved lines have no special significance, and to bring this formula in harmony with other chemical formulas we may write it thus:



This formula, then, simply symbolizes the fact that each of the six hydrogen atoms of benzene bears the same relation to the molecule.

If we examine the formula carefully with reference to the derivation of bi-substitution products, we are led to the conclusion that a compound represented by it ought to yield three classes of bisubstitution products. Numbering the hydrogen atoms thus:

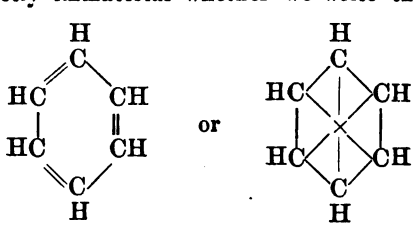


it is plain that there are three kinds of relations which any one hydrogen atom bears to the others considered individually. Thus, the relation of 1 to 2 is different from that of 1 to 3 or 1 to 4. The relation of 1 to 5 is identical with that of 1 to 3, and that of 1 to 6 is identical with that of 1 to 2. Hence, if we replace H.1 by X, and another hydrogen by another X, three different products ought to result according as we replace H.2, H.3, or H.4 by the second X. The same statements hold, whether we start with H.1 or H.2, or any of the other hydrogen atoms.

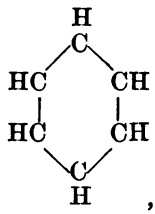
It will thus be seen that the formula is in strict harmony with the observed fact that there are but three classes of bi-substitution products of benzene.

In a similar way it can be shown that the formula is also in harmony with the fact that of the tri-substitution products there are more than three varieties, though not much weight can be attached to this as yet, as the subject has not been investigated to a sufficient extent to furnish us with a sufficient basis of facts.

There is another fact which, if interpreted by the aid of the valence hypothesis, also speaks in favor of the above formula. This formula, as given, does not account for all the bonds of carbon. We do not know what relation exists between these carbon atoms. Various formulas have been suggested with the object of showing how the bonds are disposed of, but they are all open to the serious objection that they try to express relations about which we know absolutely nothing. At the present stage of our knowledge it is perfectly immaterial whether we write the formula:

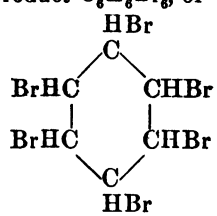


both of which are in use. It is better not to write either, but to use the simple figure above given, which does not attempt to tell the entire story, but simply to express by a symbol certain ideas to which we are led by a consideration of the facts known to us. Using, then, the simplest formula,



,

though for the argument it is immaterial which one of the three we use, the idea suggests itself that this hydrocarbon ought to be able to take up bromine; it appears to be unsaturated. If each carbon atom has the power to hold four atoms, then plainly each one ought to be able to take up one atom of bromine. By treatment with bromine, benzene ought to yield an addition-product $C_6H_6Br_6$, or



In strange accordance with this is the fact that, when benzene is treated with bromine in the sunlight, a product $C_6H_6Br_6$ is actually formed, and not $C_6H_6Br_8$, as in the case of the isomeric hydrocarbon dipropargyl.

Taking all the facts together then, it is clear that the formula given for benzene represents to the properly trained mind some facts of fundamental importance for the compound. No one claims that this formula, any more than any other in use, represents the actual arrangement of the atoms in space, or that the formula has anything whatever to do with facts of this order. But it undoubtedly does represent certain truths.

Substitution Products of Benzene.—Of mono-substitution products we have only one variety. There is only one monochlorbenzene, C_6H_5Cl; only one hydroxybenzene, or phenol, $C_6H_5.OH$; only one benzoic acid, $C_6H_5.COOH$; only one toluene, $C_6H_5.CH_3$, etc., etc. The constitution of most of these derivatives is very simple. There is a peculiarity, however, connected with those which are formed by replacing one hydrogen atom of benzene by a hydrocarbon residue.

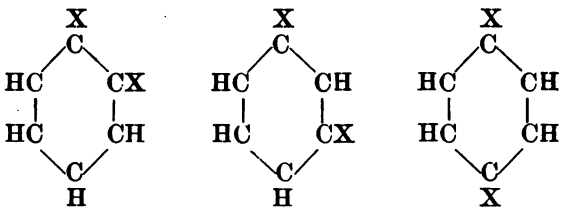
The simplest compound formed in this way is toluene, which consists of benzene in which a hydrogen atom has been replaced by the methane residue CH_3; if, instead of the residue CH_3, we introduce C_2H_5, we obtain ethylbenzene, $C_6H_5.C_2H_5$, which is plainly a homologue of toluene; so, also, the residues C_3H_7, C_4H_9, C_5H_{11}, etc., may be employed, and thus we obtain a homologous series of aromatic hydrocarbons, all of which are mono-substitution products of benzene. These may, further, all be regarded as substitution products of the hydrocarbons of the methane series. Accordingly, of toluene and ethylbenzene, which are mono-substitution products of methane and ethane respectively, only one variety is possible; while, of the next homologue, or propylbenzene, $C_6H_5.C_3H_7$, two varieties are possible, corresponding to the α- and β-mono-substitution products of propyl, or to the propyl and isopropyl compounds (which see). The main members of the series of hydrocarbons thus referred to are:

Benzene,	C_6H_6.
Toluene or methylbenzene,	C_7H_8 or $C_6H_5.CH_3$.
Ethylbenzene,	C_8H_{10} or $C_6H_5.C_2H_5$.
Propylbenzene,	C_9H_{12} or $C_6H_5.C_3H_7$.
Butylbenzene,	$C_{10}H_{14}$ or $C_6H_5.C_4H_9$.
Amylbenzene,	$C_{11}H_{16}$ or $C_6H_5.C_5H_{11}$.

Of these hydrocarbons, two kinds of mono-substitution products are possible, viz., those in which the substituting group or element is situated in the *benzene proper*, and those in which the substituting group or element is situated in the other residue. These other residues, however they may be constituted, are known as *side chains*. It is plain that substitution products of the latter kind correspond closely to those of the hydrocarbons of the methane series, and hence they need no special consideration here. If a substituting group or element enter into the benzene nucleus of any of these hydrocarbons, of course we have no longer to deal with mono-substitution products of benzene.

Bi-substitution Products.—The three classes of bi-derivatives of benzene, which we have above recognized as possible, have been designated respectively as *ortho*, *meta*, and *para compounds*, or, by others, as 1.2, 1.3, and 1.4 compounds. The former expressions are to be preferred, for

they are independent of any hypothesis concerning the positions of the substituting groups. It is usual to consider the expressions ortho and 1.2, meta and 1.3, para and 1.4, as identical, but this implies that the following formulas have been proved, while they have not been:



Ortho compound. Meta compound. Para compound.

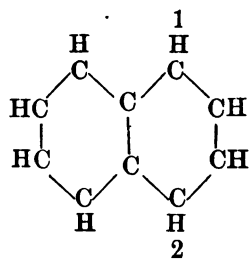
What we really know is that there are three classes of these bi-substitution products, and that the members of any one of these classes can be converted into each other, thus showing that they are allied. There are three compounds, each representing one of the three classes to which all other bi-substitution products are referred, if possible. If the constitution of any such product is unknown, it is only necessary to convert it into one of the three compounds, when the series to which it belongs is assumed to be known. The three compounds are the isomeric, bicarbonic acids of benzene, $C_6H_4\begin{matrix}COOH\\COOH\end{matrix}$, viz., phthalic, isophthalic, and terephthalic acids. All bi-substitution products which can be converted into phthalic acid are known as ortho compounds, all that can be converted into isophthalic acid are known as meta compounds, and all that can be converted into terephthalic acid are known as para compounds.

The conversion into these acids need not always be direct. If it is possible to convert a compound into another, which, in its turn, can be converted into one of the above acids, the same conclusion is drawn as in the case of a direct conversion. Of course, the accuracy of the conclusions drawn with reference to the constitution of bi-substitution products depends upon the trustworthiness of the reactions employed in effecting the conversions. Some reactions employed for this purpose have been found to give inaccurate results, that

is to say, the products resulting from an application of these reactions belong to different series from those to which the original compounds belonged. It is very probable that some compounds now classified with one series in consequence of some transformations, may be found by future investigations to belong to a different series.

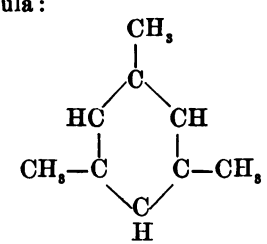
The formulas given above as representing the relative positions of the substituting groups in ortho-, meta-, and para-compounds are based upon the following facts:

It will be shown that naphthalene (which see) probably has the formula:

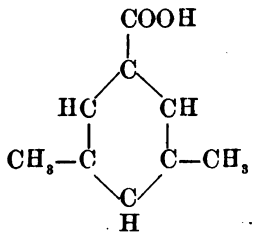


By oxidation, naphthalene yields phthalic acid. It seems probable, therefore, that the carboxyl groups in the acid have the same relative position as that of the groups numbered 1 and 2 in this formula. Consequently, ortho-compounds, or those which can be converted into phthalic acid, are assumed to have their substituting groups in the positions marked 1.2 in the benzene; or, what is the same thing, the substituting groups in ortho-compounds are combined with carbon atoms which are adjacent in the formula.

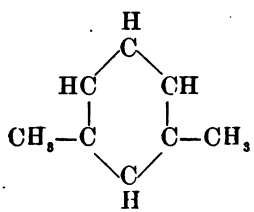
It will also be shown that mesitylene (which see) probably has the formula:



By partially oxidizing this hydrocarbon, one methyl is changed to carboxyl, and an acid is obtained of the formula:



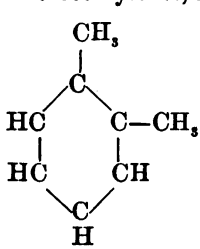
When this acid is heated under proper conditions, carbon dioxide is given off, and a hydrocarbon is obtained of the formula:



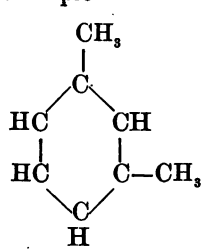
Lastly, when this hydrocarbon is oxidized, both the groups CH_3 are converted into COOH, and the product is isophthalic acid. Hence, if the formula of mesitylene is correct, that of isophthalic acid is also correct.

By exclusion, terephthalic acid becomes a 1.4 compound, and, consequently, all para-compounds are 1.4 compounds.

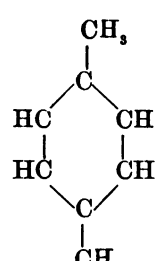
Another method of proof is founded upon determinations of the number of isomeric substitution products which can be obtained from certain bi-derivatives of benzene. Take the three xylenes, for example:



I.



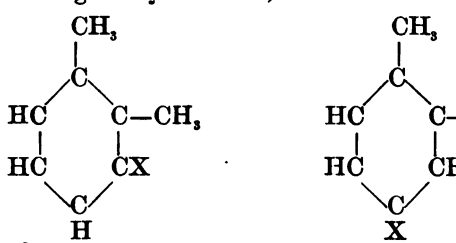
II.



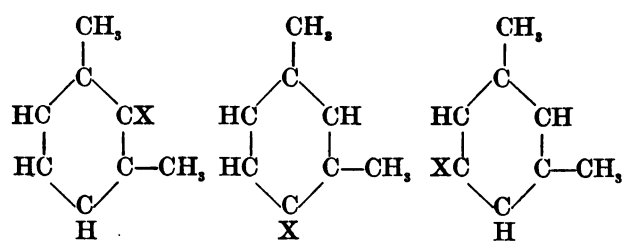
III.

There are three hydrocarbons known which can be shown to be dimethyl derivatives of benzene. The benzene hypothesis furnishes us with the three formulas, but we cannot determine by intuition which one of the formulas to give to one particular hydrocarbon, and yet, if the benzene hypothesis is of value, only one of the three formulas is assignable to any particular hydrocarbon.

An examination of formula III. will show that each of the four hydrogen atoms belonging to the benzene bears exactly the same relation to the molecule. Interpreting this formula in the simplest way, we are led to the conclusion that the compound which it represents ought to yield but one mono-substitution product with any one agent, for it should make no difference which one of the four hydrogen atoms is replaced. This is not true of the two other formulas I. and II. The compound represented by formula I. ought to yield two different mono-substitution products with any one reagent, and the compound represented by formula II. ought to yield three, thus:



Form. I.



Form. II.

It has been shown that from one of the three xylenes only one variety of mono-substitution products can be obtained, and the conclusion is drawn that to this one formula III. should be assigned. This is paraxylene, so that we are led by this method of proof to exactly the same conclusion as by the methods already considered. This method has not been fully applied in the case of the two other hydrocarbons, but sufficient is known in connection with other bi-substitution products of benzene to show that some of them yield two, and only two, kinds of derivatives by the introduction of one more substituting group, while others yield three. The former are the ortho-, the latter the meta-compounds.

It must be confessed that these proofs are not strong enough to command universal respect among chemists. As the expressions 1.2, 1.3, and 1.4 are in common usage, it is well, however, to know the grounds upon which their use is based. Some of the principal bi-substitution products of benzene are given in the following table, which shows also to which series the compounds belong:

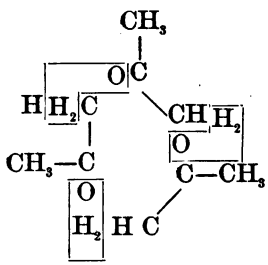
Ortho.	Meta.	Para.
Phthalic acid,	Isophthalic acid,	Terephthalic acid,
Orthoxylene,	Isoxylene,	Xylene,
Salicylic acid,	Oxybenzoic acid,	Paroxybenzoic acid,
Pyrocatechin,	Resorcin,	Hydroquinone,
Orthodinitrobenzene,	Metadinitrobenzene,	Paradinitrobenzene,
Orthobibrombenzene.	Metabibrombenzene.	Parabibrombenzene.

Tri-substitution Products.—One of the most important of the tri-substitution products of benzene is mesitylene. The formula of this hydrocarbon is C_9H_{12}. By oxidation it yields, according to the energy of the reaction, three different products. The first, mesitylenic acid, $C_8H_9.COOH$, is monobasic; the second, uvitic acid, $C_7H_6.(COOH)_2$, is bibasic; and the third, trimesinic acid, $C_6H_3.(COOH)_3$, is tribasic. All of these acids, when heated with lime, yield either benzene itself or derivatives of benzene. Hence, it is concluded that mesitylene is benzene in which three hydrogen atoms are replaced by the residue CH_3, as expressed in the formula $C_6H_3(CH_3)_3$. By oxidation each one of these groups in turn is converted into carboxyl, yielding thus the three acids above mentioned. It still remains, however, to decide what the positions of these three substituting groups in benzene are.

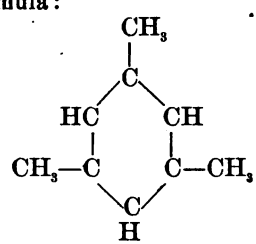
The following method of consideration leads to the formula for mesitylene given on page 214:

When acetone is treated with concentrated sulphuric acid, water is abstracted and the residues of three molecules unite to form mesitylene. It seems fair to assume that the three residues are constituted exactly the same, as they are formed under exactly the same conditions, from the same compound. If they are the same, each must be C_3H_4. Three such residues might be formed from acetone, thus:

Acetone is $CH_3—CO—CH_3$; three molecules may be arranged:



If water is abstracted in the manner indicated by the lines, we have left three residues, C_3H_4, and, if these unite, they would form a compound of the constitution represented by the following formula:



This is the formula accepted for mesitylene; and from this we conclude, as above pointed out, that meta-compounds have their substituting groups in the positions 1.3.

If this formula is carefully examined, it will be seen that each one of the three hydrogen atoms remaining in the benzene occupies a position like that occupied by the other two. Accordingly, if this formula is correct, we would expect to find that, by the introduction of one substituting group into mesitylene, only one product would be formed. This has actually been found to be true.

Besides mesitylene, there are many tri-substitution products of benzene known, containing such elements as Cl, Br, I, and such groups as NO_2, NH_2, SO_2OH, etc. The principle, according to which the position of the substituting groups in these compounds is determined, is this: One of the groups is split off, and the constitution of the resulting bi-substitution product is determined as above; then, from the original compound some other group is split off, and the constitution of the bi-substitution product resulting in this case also determined. We are thus able to judge of the positions of the three groups with reference to each other. There are not many compounds, however, which can be subjected to this kind of examination with satisfactory results, so that the constitution of these tri-derivatives is not nearly as well known as that of the bi-derivatives.

Peculiar Benzene Derivatives.—Among benzene derivatives, we find three classes which are not represented among the fatty bodies, and hence they require some attention here. These are the *phenols, quinones,* and *azo-bodies.*

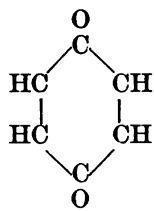
Phenols.—Phenols are the hydroxy-derivatives of benzene and its homologues, formed by the introduction of hydroxyl in the place of hydrogen in benzene. The corresponding compounds of the hydrocarbons of the methane series are all alcohols, either primary, secondary, or tertiary. The phenols are, however, not alcohols in the sense in which that term has been used up to the present. By oxidation they yield neither aldehydes, acids, nor ketones. If, however, by the expression tertiary alcohol we mean any compound which contains the grouping C(OH), then the phenols are all tertiary alcohols. It is, perhaps, better to restrict the use of the name alcohol to the hydroxyl derivatives of the marsh-gas hydrocarbons.

The presence of hydroxyl in phenols can be proved in the same way that it was proved for other bodies containing hydroxyl.

There are monacid phenols, containing only one hydroxyl; diacid phenols, containing two hydroxyls; triacid phenols, containing three hydroxyls; etc.

Quinones.—The quinones are derived from benzene and its homologues by the introduction of two atoms of oxygen

in the place of two hydrogen atoms in benzene. Thus the simplest quinone has the formula $C_6H_4O_2$. The two oxygen atoms are supposed to form a bivalent group, —O—O—, by combining with each other by means of one of their affinities each. Most quinones are derived from para-compounds by oxidation, as from hydroquinone, and hence it is concluded that the hydrogen atoms replaced by the bivalent group —O—O— in the formation of quinones usually occupy the para-position with reference to each other. Accordingly, if the para-position is 1.4, the formula of ordinary quinone is

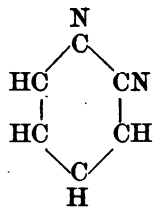


All quinones are supposed to be similarly constituted, though it is still a question whether all quinones are para-compounds. Certain experiments seem to indicate that there are quinones which belong to the meta-series.

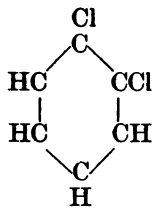
Azo- and Diazo-bodies.—These bodies, as their names imply, are nitrogen derivatives. They are derived from benzene and its homologues by the substitution of nitrogen for hydrogen. We need only consider those which are derived from benzene, as the others are very closely related to them. The diazo-derivatives of benzene are obtained from the salts of aniline or amidobenzene, $C_6H_5.NH_2$, by the action of nitrous acid. Thus aniline nitrate, $C_6H_5.NH_2.HNO_3$, yields diazobenzene nitrate; aniline sulphate, $(C_6H_5.NH_2).H_2SO_4$, yields diazobenzene sulphate, etc.

If we consider simply the empirical formulas of the salts of diazobenzene thus obtained, we find that they differ from the aniline salts in containing $C_6H_4N_2$, in the place of $C_6H_5NH_2$. The salts consist of the acids plus this group. Thus the nitrate is $C_6H_4N_2.HNO_3$; the sulphate is $C_6H_4N_2.H_2SO_4$, etc. These formulas are not supposed, however, to represent the constitution of the salts. If the group $C_6H_4N_2$ actually existed in these diazo-bodies, it is

plain that they would be bi-substitution products, that is to say, two hydrogen atoms of benzene would be replaced by two nitrogen atoms. It was at first supposed that each of these nitrogen atoms played the part of a univalent element, and the diazo-compounds were looked upon as analogous to bichlorbenzene, binitrobenzene, etc., thus:



Diazobenzene.



Bichlorbenzene.

It was soon found, however, that, when the diazo-bodies are decomposed, they generally yield derivatives of benzene in which the group C_6H_5 is undoubtedly present. Thus the following decompositions of diazobenzene sulphate yield, in each case, a derivative containing C_6H_5:

When boiled with alcohol, the products are benzene, nitrogen, and sulphuric acid:

$$\frac{C_6H_5.N_2.HSO_4}{H \quad H} \text{ yield } \begin{array}{c|c|c} C_6H_5 & N_2 & HSO_4 \\ H & & H \end{array}.$$

When boiled with water, the products are phenol, nitrogen, and sulphuric acid:

$$\frac{C_6H_5.N_2.HSO_4}{OH \quad H} \text{ yield } \begin{array}{c|c|c} C_6H_5 & N_2 & HSO_4 \\ OH & & H \end{array}.$$

When treated with hydriodic acid, the products are iodbenzene, nitrogen, and sulphuric acid:

$$\frac{C_6H_5.N_2.HSO_4}{I \quad H} \text{ yield } \begin{array}{c|c|c} C_6H_5 & N_2 & HSO_4 \\ I & & H \end{array}.$$

Other reactions indicate as well that the group C_6H_5 is present in the diazo-compounds. But, if this group is present, the two nitrogen atoms must be so combined that they can take the place of one hydrogen atom. Now, if two nitrogen atoms, which have the same valence, be combined,

they must either form a neutral group with all its affinities satisfied, or a group which is at least bivalent. Such a bivalent group will be formed, for instance, if two nitrogen atoms were to be united by means of two affinities each, thus, —N=N—. If this group should replace one hydrogen atom of benzene, the constitution of the resulting compound would be C_6H_5—N=N—. Such a compound would be unsaturated. No compound of the formula $C_6H_5N_2$ has been obtained, but all the derivatives of diazobenzene can be explained on the supposition that they are derived from the compound C_6H_5—N=N.

Accepting the group C_6H_5—N=N— as the foundation of the diazo-compounds, these may be formulated as follows:

C_6H_5—N=N—Br,	diazobenzene bromide,
C_6H_5—N=N—NO_3,	diazobenzene nitrate,
C_6H_5—N=N—HSO_4,	diazobenzene sulphate,
C_6H_5—N=N—OK,	diazobenzene potassa,
C_6H_5—N=N—NH(C_6H_5),	diazobenzene diamidobenzene.

Azobenzene is formed by the reduction of nitrobenzene. Its formula is $C_{12}H_{10}N_2$. As nitrobenzene contains the group C_6H_5 combined with N, we can assume that azobenzene consists of two such groups C_6H_5—N=. If these combine in the simplest manner, we would have the formula $\begin{matrix} C_6H_5—N \\ \| \\ C_6H_5—N \end{matrix}$, expressing the constitution of azobenzene. This is the formula which is now generally accepted.

According to this, the azo-compounds are very closely related to the diazo-compounds. Both contain the group —N=N— in combination with C_6H_5. In reality, the azo-compounds differ very much in their chemical conduct from the diazo-compounds. The decompositions which they undergo take place in a manner entirely different from that already noticed as characterizing the decomposition of diazo-compounds.

This difference has led some chemists to abandon the formulas above given for the diazo-compounds, and to propose others in their place. The compounds are supposed to be ammonium compounds of the general formula,

$R—N—R'$
$\|\|\|$
N . They contain one quinquivalent and one trivalent nitrogen atom. The relation between aniline nitrate and diazobenzene nitrate is shown thus:

C_6H_5
$|$
$N—O—NO_2$;
$\|\|\|$
H_3
Aniline nitrate.

C_6H_5
$|$
$N—O—NO_2$.
$\|\|\|$
N
Diazobenzene nitrate.

It remains to be determined, by future experiments, which of the formulas for diazo-compounds is correct. Up to the present there exist no good proofs of either.

Phenylmethanes.

The homologues of benzene are of two kinds, as was shown (see p. 212). They are obtained either by introducing one, two, or more methyl groups into benzene, or by introducing homologous groups of marsh-gas hydrocarbons into benzene. Just as we can introduce methyl groups into benzene, so also we can introduce the group phenyl, C_6H_5, into methane. Thus, we may get the hydrocarbons:

Phenyl-methane, $CH_3.C_6H_5$ (identical with toluene);
Diphenyl-methane, $CH_2(C_6H_5)_2$;
Triphenyl-methane, $CH(C_6H_5)_3$; and
Tetraphenyl-methane, $C(C_6H_5)_4$.

Of the three last members, triphenyl-methane has been most carefully studied. It is the mother-substance of two important groups of compounds, the *aniline dyes* and the *phthaleins*.

The hydrocarbon is easily obtained by bringing chloroform, $CHCl_3$, and benzene, C_6H_6, together in the presence of aluminium chloride (reaction of Friedel and Crafts). In some way not understood, the chloride causes the two to act upon each other as represented in the equation:

$$CHCl_3 + 3C_6H_6 = CH(C_6H_5)_3 + 3HCl.$$

Rosaniline and Pararosaniline.—The aniline dyes are for the most part comparatively simple derivatives of rosaniline

or pararosaniline. Pararosaniline is formed by oxidizing a mixture of aniline, $C_6H_5.NH_2$, and paratoluidine,

$$C_6H_4\begin{cases}CH_3\\NH_2\ (p)\end{cases}:$$

$$\underset{\text{Aniline.}}{2C_6H_7N} + \underset{\text{Toluidine.}}{C_7H_9N} + 3O = \underset{\text{Pararosaniline.}}{C_{19}H_{17}N_3} + 3H_2O.$$

Rosaniline is formed in a similar way:

$$\underset{\text{Aniline.}}{C_6H_7N} + \underset{\text{Toluidine.}}{2C_7H_9N} + 3O = \underset{\text{Rosaniline.}}{C_{20}H_{19}N_3} + 3H_2O.$$

Pararosaniline has been made from triphenylmethane by reactions which show the relations between the two compounds.

By treatment with nitric acid the hydrocarbon yields a trinitro-derivative. The same product is formed by bringing chloroform and nitro-benzene together in the presence of aluminium chloride, thus:

$$CHCl_3 + 3C_6H_5(NO_2) = \underset{\text{Trinitro-triphenyl-methane.}}{CH(C_6H_4.NO_2)_3} + 3HCl.$$

By reduction the trinitro-product is converted into the corresponding triamido-derivative, $CH\begin{cases}C_6H_4.NH_2\\C_6H_4.NH_2\\C_6H_4.NH_2\end{cases}$ = $C_{19}H_{19}N_3$. By gentle oxidation this body, known as *paraleucaniline*, loses two hydrogen atoms, and pararosaniline is formed. It has been found that pararosaniline is also formed when the compound $C(OH)\begin{cases}C_6H_4.NH_2\\C_6H_4.NH_2\\C_6H_4.NH_2\end{cases}$, triamido-triphenyl carbinol, is set free from its salts. The carbinol loses water and yields a sort of anhydride which is pararosaniline. The simplest view held in regard to the constitution of the latter substance is represented in the formula

$$C\begin{cases}C_6H_4.NH_2\\C_6H_4.NH_2\\C_6H_4.NH\end{cases} = C_{19}H_{17}N_3\ .$$

By a consideration of similar facts we are led to the formula

$$C\begin{cases} C_6H_3\begin{cases}CH_3\\NH_2\end{cases} \\ C_6H_4.NH_2 \\ C_6H_4.NH \end{cases} = C_{20}H_{19}N_3 \text{ for rosaniline.}$$

Phthaleins.—The phthaleins are bodies which are formed by treating a mixture of phthalic anhydride, $C_8H_4O_3$, and some phenol with a dehydrating agent. The simplest representative of the class is phenol-phthalein, which is made by heating a mixture of ordinary phenol and phthalic anhydride with sulphuric acid:

$$\underset{\text{Phenol.}}{2C_6H_6O} + \underset{\substack{\text{Phthalic}\\\text{anhydride.}}}{C_8H_4O_3} = \underset{\text{Phenol-phthalein.}}{C_{20}H_{14}O_4} + H_2O.$$

The phthaleins are derivatives of triphenyl-methane, as has been shown by the following transformations.

The chloride of phthalic acid, $C_8H_4O_2Cl_2$, when treated with benzene in the presence of aluminium chloride, yields a product known as diphenyl-phthalide:

$$\underset{\text{Phthalyl chloride.}}{C_8H_4O_2Cl_2} + 2C_6H_6 = \underset{\text{Diphenyl-phthalide.}}{C_8H_4O_2(C_6H_5)_2} + 2HCl.$$

When boiled with sodium hydroxide, diphenyl-phthalide is transformed into an acid, triphenylcarbinol-carbonic acid.

$$C_8H_4O_2(C_6H_5)_2 + H_2O = C_8H_6O_3(C_6H_5)_2 \text{ or } C_7H_5O\begin{cases}COOH\\(C_6H_5)_2\end{cases}$$

When treated with zinc dust, this acid loses oxygen:

$$C_7H_5O\begin{cases}COOH\\(C_6H_5)_2\end{cases} + H_2 = C_7H_5\begin{cases}COOH\\(C_6H_5)_2\end{cases}.$$

The product, triphenylmethane-carbonic acid, when distilled with baryta, loses carbon dioxide and yields triphenylmethane. It is hence to be regarded as a simple hydroxyl derivative of triphenylmethane, $CH\begin{cases}C_6H_5\\C_6H_5\\C_6H_4.COOH\end{cases}$.

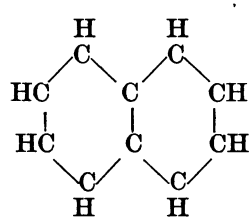
In accordance with this conclusion, the other substances in the series should be represented by the following formulas: Triphenylcarbinol-carbonic acid, $C(OH)\begin{cases}C_6H_5\\C_6H_5\\C_6H_4.COOH\end{cases}$; diphenyl-phthalide, $C\begin{cases}C_6H_5\\C_6H_5\\C_6H_4.CO\end{cases}$ (O).

Phenol-phthalein is derived from the last body by the introduction of two hydroxyls, and is represented by the formula $C\begin{cases} C_6H_4.OH \\ C_6H_4.OH \\ C_6H_4.CO. \\ \quad\quad\quad\

be replaced by the cyanogen group, and the latter then converted into carboxyl. Thus there is obtained an acid, $C_6H_4\begin{cases}CO.COOH\\NH_2\end{cases}$. This loses water very readily, and the anhydride thus formed, which may be represented by the formula $C_6H_4\begin{cases}C\,O.C\,O\\NH—\end{cases}$, is isatine.

NAPHTHALENE.

The hydrocarbon naphthalene has the formula $C_{10}H_8$. It is considered to be formed by the union of two benzene residues in such a way that, while the compound really contains the two residues, two of the carbon atoms are common to both residues. This is the fundamental idea in the prevailing view regarding the constitution of naphthalene. It is expressed thus:



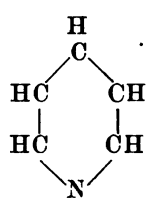
Assuming the formula for benzene to be correct, this is the only possible formula for naphthalene. It is based on the following facts: There is a derivative of naphthalene known as dichlornaphthoquinone, which has the formula $C_{10}H_4Cl_2O_2$. When this substance is oxidized, it yields phthalic acid, which is a bi-substitution product of benzene. We see thus that those carbon atoms in dichlornaphthoquinone which are not in combination with chlorine form a benzene nucleus, so that we might write the formula of the compound $C_6H_4.C_4Cl_2O_2$. This formula does not tell us in what manner the atoms $C_4Cl_2O_2$ are united, but by the aid of another experiment this can be determined.

When dichlornaphthoquinone (the substance used in the preceding experiment) is treated with phosphorus pentachloride, it is converted into pentachlornaphthalene, the formula of which, according to what was said above, is $C_6H_3Cl.C_4Cl_4$. By analogy, we would expect this compound by oxidation to yield monochlorphthalic acid; it, how-

ever, yields tetrachlorphthalic acid. This shows that the four carbon atoms which are in combination with chlorine form part of a benzene nucleus, as well as the other carbon atoms of naphthalene. It is thus proved that in naphthalene there are two benzene nuclei. The only formula which agrees with this fact is the one above given.

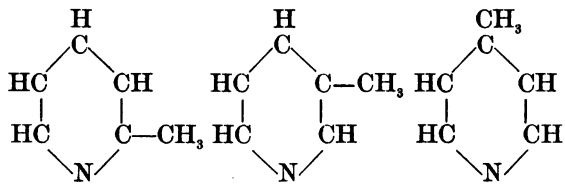
The derivatives of naphthalene resemble those of benzene, and much that has been said concerning the latter holds good in regard to the former. All the hydrogen atoms of naphthalene may be replaced by substituting groups or elements, and thus, as will be readily seen, a large number of substitution products may be obtained. The possibilities for instances of isomerism are greater in the case of naphthalene than in the case of benzene, but the principles underlying the isomerism are essentially the same as those which we have already considered in connection with the isomeric substitution products of benzene.

Pyridine and Quinoline.—A number of bases of the general formula $C_nH_{2n-5}N$ have been isolated from bone-oil and made in other ways. The simplest one is pyridine, C_5H_5N. The others are homologous with it. Pyridine is a very stable compound, differing markedly in its chemical conduct from the common ammonia bases. With reference to the higher members of the series, it conducts itself very much as benzene towards its homologues. By oxidation, its methyl derivatives yield corresponding carbonic acids. For example: toluene or methyl benzene, $C_6H_5.CH_3$, yields benzoic acid, $C_6H_5.COOH$. So, also, picoline or methylpyridine, $C_5H_4(CH_3)N$, yields pyridine-carbonic acid, $C_5H_4N.COOH$, etc. While the facts known concerning pyridine are not sufficient to justify the expression of a very decided opinion regarding its structure, they nevertheless speak in favor of a structure similar to that of benzene. If we imagine one of the CH groups of benzene to be replaced by a nitrogen atom, the resulting compound would have the formula

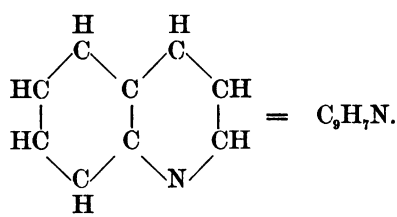


$= C_5H_5N$.

This formula represents the working hypothesis regarding the structure of pyridine. Thus far, the cases of isomerism studied are in accordance with this formula. There are, for example, three mono-methyl derivations of pyridine, and three corresponding mono-carbonic acids. The formula suggests the existence of these three varieties. The three methyl derivatives should be represented thus:



Quinoline, C_9H_7N, is the first member of a series of bases of the general formula $C_nH_{2n-11}N$, which somewhat resemble the pyridine bases. Quinoline is supposed to bear a relation to naphthalene, similar to that which pyridine bears to benzene—a conception represented by the formula:



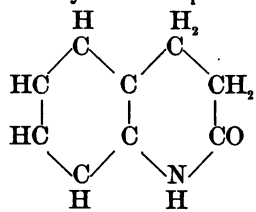
$= C_9H_7N.$

The method of preparation which admits perhaps most easily of interpretation is the following:

Cinnamic acid, as has been shown, is the carboxyl derivative of styrene, $C_6H_5.CH<>CH.COOH$. This takes up hydrogen and becomes hydrocinnamic or phenylpropionic acid, $C_6H_5.CH_2CH_2.COOH$. An ortho-amido-derivative of this acid has been made, the formula of which is $C_6H_4\begin{cases} CH_2.CH_2.COOH \\ NH_2 \end{cases}$. This loses water readily and

yields an anhydride, $C_6H_4\begin{cases}CH_2.CH_2.CO\\NH\text{———}\end{cases}$ known as hydrocarbostyril.

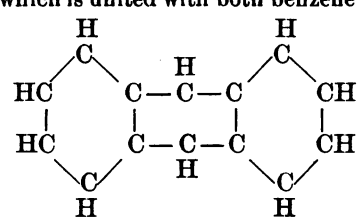
Hydrocarbostyril may also be represented by the formula



which is in principle identical with the first formula. When this substance is treated with phosphorus pentachloride, dichlorquinoline is formed. While it is not possible to say exactly how this reaction takes place, it indicates that between hydrocarbostyril and quinoline there is some close relationship, which is best accounted for by the above formulas.

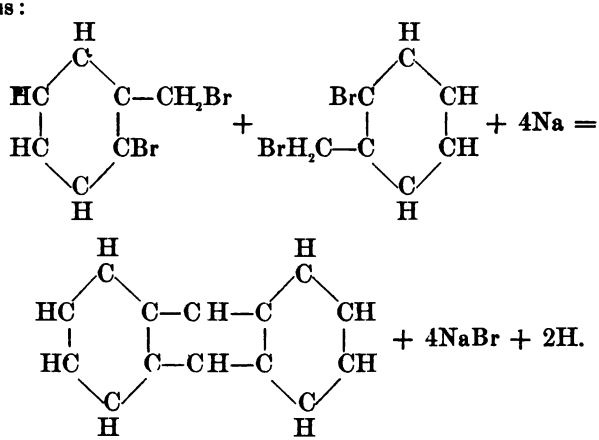
Anthracene.

Anthracene, like naphthalene and benzene, is the mother-substance of a large group of compounds. Its formula is $C_{14}H_{10}$. In regard to its constitution, the view is now commonly held that it consists of two benzene residues, C_6H_4, held together by means of the group $\begin{matrix}|&|\\HC—CH\\|&|\end{matrix}$, each carbon atom of which is united with both benzene residues, thus:



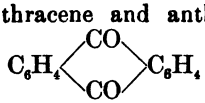
This formula is based, in the first place, on the similarity in the chemical conduct of benzene, naphthalene, and anthracene. Further, a synthesis of anthracene has been effected from orthobrombenzyl bromide, $C_6H_4\begin{cases}CH_2Br\\Br\end{cases}$.

When this compound is treated with sodium, one of the products is anthracene. The reaction may be represented thus:

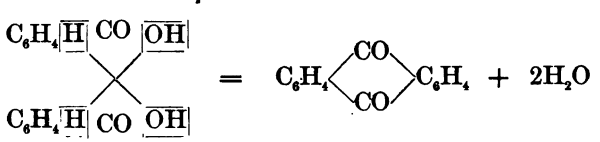


This reaction not only throws light upon the general character of anthracene, but it shows further that the linking groups CH are connected with the benzene residues in the ortho-position.

The above formula shows the relation between anthracene and anthraquinone, which appears to be

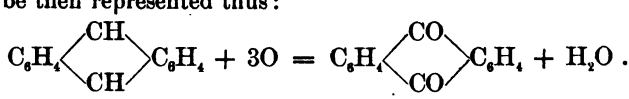


. The latter formula best explains the formation of anthraquinone from benzoic acid, and the formation of benzoic acid from anthraquinone. The former transformation is represented thus:



2 molecules Benzoic acid. Anthraquinone.

The formation of anthraquinone from anthracene should be then represented thus:



According to these interpretations, anthraquinone is a double acetone. It has been suggested, further, that all quinones are nothing but double acetones. (See Quinones, p. 219.)

Other hydrocarbons allied to naphthalene are pyrene, chrysene, and phenanthrene. These have not been investigated very fully as compared with naphthalene and anthracene themselves. All of these three undoubtedly contain benzene residues as essential parts of their molecules, but there is still some doubt in regard to the manner in which these residues are united.

Retrospect.

A study of the preceding chapters on constitution will show that no absolute meaning is to be attached to the word. Constitutional formulas are those which suggest certain reactions and recall analogies. The formula CH_3—OH does not mean that hydroxyl (OH) is necessarily present in the compound, or that CH_3 is present, but that the different parts of the compound bear such relations to each other that when the compound is decomposed it acts as if the parts were united as the formula indicates. The formula suggests possibilities; it may not represent realities.

The methods thus far considered for determining the constitution of compounds are chemical methods. They depend upon the study of chemical conduct. If we find that two compounds conduct themselves in the same general way, the formulas call this analogy to mind. If we assume a certain grouping in the one, we must assume a similar grouping in the other.

The question whether a study of the physical properties of compounds can throw any light upon the constitution of the compounds, now naturally suggests itself. A great deal of attention has been paid to the subject of late, and a brief account of some of the methods employed and the results reached will now be given.

Determination of the Constitution of Chemical Compounds by Physical Methods.

Specific Volumes.—By the *specific volume* or *molecular volume* of a substance is meant a figure obtained by dividing

the specific gravity of the substance in the form of liquid into the molecular weight. Thus, the specific gravity of ordinary alcohol at the boiling temperature is 0.736; the molecular weight is $24 + 6 + 16 = 46$; the specific volume is $\frac{46}{0\,736} = 62.5$.

A study of the specific volumes of a large number of substances has shown that a close connection exists between the figures and the constitution of the bodies. The specific gravities must be determined under strictly analogous conditions, in order that they may be comparable. The figures used are those found at the boiling-points of the liquids. Kopp first pointed out that the following definite relations exist:

1. *In many instances differences in specific volume are proportional to differences in corresponding chemical formulas.* Thus a difference of CH_2 in a homologous series corresponds to a difference of about 22 in the specific volume, or $(CH_2)\ x = 22\ x$. On comparing the specific volumes of similarly constituted haloid compounds, it is seen that the substitution of n atoms of bromine for an equal number of chlorine atoms increases the specific volume by $5n$.

2. *Isomeric and metameric liquids have, as a rule, the same specific volume.* Exceptions are exhibited by certain oxygen and sulphur compounds.

3. *The substitution of an atom of carbon for two of hydrogen makes no alteration in the specific volume of members of certain groups of organic liquids.*

On the basis of his observations Kopp was able to calculate certain fundamental values for the specific volumes of the elements in combination. These values are, as a rule, constant for any particular element: thus, carbon has invariably the value 11; hydrogen, that of 5.5. Exceptions are observed in the case of the chemical analogues oxygen and sulphur. Each of these bodies has two values, depending, it would seem, on its mode of combination, or on its relation to the remaining atoms in the molecule. For example: acetone and allyl alcohol have each the empirical formula, C_3H_6O, but the specific volume of acetone is 78.2, whilst that of allyl alcohol is 73.8. As expressed in the ordinary formulas the affinities of the oxygen in acetone are wholly satisfied by the carbon, whereas in allyl alcohol a moiety of the combining value would seem to be satisfied by carbon, and the

remainder by hydrogen. It appears, then, that when oxygen is united to an element by both its affinities its specific volume is 12.2; when it is attached by only one combining unit its specific volume is 7.8. The corresponding values for sulphur are 28.6 and 22.6.*

Assuming the conclusions of Kopp to be correct, a method is given for determining in what condition oxygen is present in a compound. An illustration will make the application of the method clear. Suppose that a compound of the formula C_2H_4O has the specific gravity 0.773. The specific volume is $\frac{44}{0.773} = 56.9$. Calculating the specific volume according to Kopp's rule, and accepting his values for carbon and hydrogen, viz.: C = 11; H = 5.5, we have $V(C_2H_4O) = 2 \times 11 + 4 \times 5.5 + x$, in which x represents the specific volume of the oxygen. But the specific volume of the compound found by experiment is 56.9; hence we have $2 \times 11 + 4 \times 5.5 + x = 56.9$; $x = 12.9$.

The specific volume of oxygen in the compound under consideration is thus shown to be 12.9, or approximately the value assigned to oxygen combined with carbon by both affinities. Thus the presence of the group —CO— is proved by this method.

A thorough examination of all the facts on record bearing upon the subject of specific volumes has led Lossen to conclude that the rule of Kopp is not strictly true; that the specific volumes of the elements vary somewhat according to the class to which the compound into which they enter belongs. He considers it probable that certain figures will be found to express the specific volumes of the elements as they occur in different classes of compounds, and that these figures will be very similar to those given by Kopp. The whole subject of specific volumes is now under investigation.

Molecular Refraction.—The study of the refracting power of different organic liquids has led to results of interest, which show that there is a close connection between this power and the constitution of the bodies. In order that the results may be comparable the *refraction-equivalent* is determined. This is represented by the expression $P\left(\frac{n-1}{d}\right)$, in which P is the molecular weight of the body, n the index of refraction, and d the density of the

* See Thorpe, Journal of the Chemical Society, XXXVII., 141.

body. The index is determined for four different lines of the spectrum obtained from the sodium light, and from the light emitted by hydrogen in a Geissler's tube.

Landolt has shown that, in general, bodies of the same composition have the same refraction equivalent, the value of this equivalent being dependent upon the number and kinds of atoms present in a molecule, rather than upon the arrangement of these atoms. Each atom must then have its own refraction-equivalent, and, if we know what this is, we can calculate the equivalent for a body of any given composition. In order to determine the values for carbon, hydrogen, and oxygen, Landolt made use of several methods, the principle of which will appear from the following illustration. Two compounds were compared with each other, the compositions of which differed by one atom of carbon, two atoms of hydrogen, or one of oxygen, the difference in the molecular refraction of the two bodies giving the refraction equivalent of the element. Thus, the refraction-equivalent ($P\frac{n-1}{d}$) of methyl alcohol is 13.17; that of aldehyde is 18.58. The difference in composition is one carbon atom. It is hence concluded that the difference in the molecular refraction of the two bodies is due to the one carbon atom, or that the atomic refraction of carbon is 5.41. In the same way aldehyde and ethyl alcohol, which differ in composition by two hydrogen atoms, show a difference in molecular refraction of 2.12; and it is concluded that the atomic refraction of hydrogen is half of 2.12. By comparing aldehyde and acetic acid, which differ by one atom of oxygen, the atomic refraction of oxygen is found to be 2.53.

		$P(\frac{n-1}{d})$	*Difference.*
Difference in Composition C_1.			
Methyl alcohol,	CH_4O, . .	13.17	5.41
Aldehyde,	C_2H_4O, . .	18.58	
Difference in Composition H_2.			
Aldehyde,	C_2H_4O, . .	18.58	2.12
Ethyl alcohol,	C_2H_6O, . .	20.70	
Difference in Composition O_1.			
Aldehyde,	C_2H_4O, . .	18.58	2.53
Acetic acid,	$C_2H_4O_2$, . .	21.11	

As a mean of a large number of experiments, the follow-

ing values were obtained for the atomic refraction of the three elements:

$$C = 5;\ H = 1.3;\ O = 3.$$

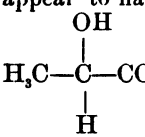
By means of these figures, then, we can calculate the refraction-equivalent of any given body composed of these three elements. On comparing the calculated values with those determined by experiment, Brühl found that the two are equal in a large number of cases, but that, in a number of other cases, the values found by experiment are greater than those calculated. More careful examination of the subject showed that all the bodies which form exceptions to the general rule belong to the class of unsaturated compounds, and that all saturated compounds give results in harmony with the rule.

The occurrence in a compound of the condition known as double linkage between carbon atoms (see pp. 91 and 202) causes an increase of 2 in the value of the molecular refraction above that obtained by calculation.

So, also, the presence of carbonyl, CO, causes an increase in the molecular-refraction above the value calculated for oxygen in the singly linked condition, as in C—O—H.

It is plain that, if these rules can be shown to be well founded, a method is given for determining whether double linkage between carbon atoms, or between carbon and oxygen, exists in compounds under examination.

Polarization Phenomena.—Reference has been made to the hypothesis of Le Bel and van't Hoff (see p. 191) to account for some cases of isomerism which cannot be explained by any of the commonly accepted hypotheses. Thus we have paralactic and ordinary lactic acids, both of which appear to have the constitution expressed by the formula



$H_3C—C—COOH$. They differ from each other, however, in their conduct towards polarized light. While the latter is optically inactive, the former is strongly dextro-rotatory. According to the hypothesis, when a carbon atom unites with four radicals of different kinds, an asymmetrical molecule is formed, and a compound made up of such molecules

may have rotatory power. If, in a molecule represented by the general formula, $E-\overset{\overset{A}{|}}{C}-\underset{\underset{D}{|}}{B}$, in which the letters A, B, D, and E stand for different atoms or groups, we conceive the carbon atom to be in the centre, and the four radicals A, B, D, and E at the four angles of a tetrahedron, there are two ways in which the radicals can be arranged with reference to the carbon atom. Arranging the constituents of the molecule in any way, the other possible way is found by regarding the reflection of the arrangement in a mirror. Given any compound with a carbon atom in combination with four different radicals, and we have the possibility of two isomeric forms which ordinary formulas cannot account for.

In the two lactic acids we have the condition referred to as shown by the formula $H_3C-\overset{\overset{OH}{|}}{C}-\underset{\underset{H}{|}}{COOH}$, in which the central carbon atom is in combination with 1)OH ; 2)COOH ; 3)H ; and 4)CH_3, and is consequently asymmetrical.

The above hypothesis applies to tartaric acid, malic acid, active amyl alcohol, mannite, and many other substances.

While a great deal more work will be necessary before the hypothesis can be regarded as completely established, our knowledge on the point at present may be fairly summed up in the two following sentences :

1. Optically active substances always contain one or more asymmetrical carbon atoms.

2. Bodies which do not contain asymmetrical carbon atoms have no rotatory power.

Heat Phenomena.—A great deal of attention has been given to the heat phenomena exhibited in chemical transformations, and many conclusions of value have been drawn from the experiments. As yet, however, these conclusions have very little bearing upon the subject of the constitution of chemical compounds, in the sense, at least, in which this expression has been used in this book. But, enough has

been done to show that, by studying these heat phenomena, analogies may be shown to exist between compounds of similar constitution. Isomeric substances evolve different quantities of heat in combustion. They differ from each other in the amounts of energy they contain. It appears probable that a thorough study of the heat phenomena may furnish us with a more rational basis for the classification of chemical compounds than any we now possess, and that it may completely change our mode of looking at the compounds and chemical reactions. Up to the present, however, the influence exerted by this kind of study has not been very marked.

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